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A LABORATORY MANUAL OF ELEMENTAL

QUALITATIVE CHEMICAL ANALYSIS

FOR STUDENTS OF
MEDICINE, DENTISTRY, PHARMACY,
AND SCIENCE

BY

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1918

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B64
1918

TO HIS
Mother
WHOSE UNTIRING DEVOTION TO DUTY, WILLING
SACRIFICES, AND NOBILITY OF CHARACTER
HAVE BEEN A CONTINUOUS SOURCE
OF INSPIRATION
THIS VOLUME IS FONDLY DEDICATED
BY THE
AUTHOR

QUALITATIVE CHEMICAL ANALYSIS

PART I

THE METALS OR CATIONS

CHAPTER I

Introduction

1. The course of instruction followed in this manual presupposes that the student has already a fair knowledge of the fundamental principles of physical and chemical theory. He should be familiar also with the simple operations of Solution, Crystallization, Neutralization, Precipitation, Filtration, Decantation, Washing, Evaporation, Distillation, Ignition, Sublimation, Fusion and Deflagration, and must become familiar with the use of the blowpipe.

2. The apparatus required by each student is as follows:

One Ring-stand with two or more Rings.
One Iron Tripod.
One Bunsen Burner with rubber tubing.
One Blowpipe Tube for Bunsen Burner.
One Blowpipe.
One Stoddart's Clamp.
Two Pieces of Wire Gauze.
One Triangular File.
One Rat-tail file.
One Piece of Wood Charcoal.
One Piece of Platinum Foil, 1½ inches square.
One Piece of Platinum Wire, 3 inches long mounted in a glass rod.
One Piece of Cobalt glass.

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One small Mortar and Pestle.
Two Porcelain Evaporating Dishes.
Three 2-inch Glass Funnels.
Twelve Test-tubes, ⅝ x 6 inches.
One Wooden Test-tube Rack.
Two Test-tube Brushes.
Three Glass Beakers, 150 Cc.
Two Watch-glasses, 2 inch.
One Hydrogen Sulphid Generator.
One Wash-bottle.
One Glass Spatula.
One Porcelain Crucible.
Four Glass Rods, 8 inches long.
Filter-papers, 3 inches.
One Pipestem Triangle.
One Water-bath.
Hard Glass Tubing.
One Calcium Chlorid Tube.
One Piece White Wax.
One Small Porcelain Boat.
One Aspirating Apparatus.

3. Substances which indicate the presence of other substances by some striking phenomena, such as a change in color, liberation of a gas, formation of a precipitate, are known as "REAGENTS." The following list includes the substances and solutions needed for the work as outlined in this manual.

GASES

*Chlorin
*Hydrogen Sulphid

LIQUIDS

SOLVENTS

Alcohol, Ethyl, 95%
Carbon Disulphid
Chloroform
Ether
Glycerin
Water, Distilled

SOLUTIONS

Acid, Acetic, Dil., 34.6%
" *Chloroplatinic, 10.3 Gm. in 100 of Water
" Hydrochloric, Conc., S/G., 1.2 (38%)
" Hydrochloric, Conc., *Arsenic-free*
Acid Hydrochloric, 10%
" Nitric, Concentrated, S/G., 1.42 (69.8%)
" Nitric, 32.3%
" Oxalic, 126 Gm. to 1 L.
" Sulphuric, Concentrated, S/G., 1.84 (96%)

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*See page 21.

Acid Sulphuric, 24.8%
" Sulphurous (Sat. Sol. of SO_2)
" Tartaric, 150 Gm. to 1 L.
Albumin
Alcohol, Ethyl, 50%
*Ammonium Acetate
" Aluminium Sulphate, 59 Gm. to 1 L.
" *Carbonate
" Chlorid, 107 Gm. to 1 L.
" Hydroxid, 28% and 10%
" *Molybdate
" Nitrate, 160 Gm. to 1 L.
" *Polysulphid
" Oxalate, Sat. Sol.
" Sulphate, 132 Gm. to 1 L.
" *Sulphid
Antimony Chlorid, 25 Gm., 250 Cc. HCl, Water to 1 L.
Barium Chlorid, 122 Gm. to 1 L.
" Hydroxid, Sat. Sol.
" Nitrate, 65 Gm. to 1 L.
Bismuth Chlorid, 26 Gm. to 1 L.
" Nitrate, 40 Gm. to 1 L.
Borax, 96 Gm. to 1 L.
Bromin Water, Sat. Sol.
Cadmium Nitrate, 77 Gm. to 1 L.
" Sulphate, 64 Gm. to 1 L.
Calcium Chlorid, 56 Gm. to 1 L.
" Hydroxid, Sat. Sol.
" Sulphate, Sat. Sol.
Chlorin Water, Sat. Sol.
Chromium Chlorid, 39.5 Gm. to 1 L.
Cobalt Nitrate, 36 Gm. to 1 L.
" Sulphate, 32 Gm. to 1 L.
Copper Sulphate, 63 Gm. to 1 L.
Ferric Chlorid, 90 Gm. to 1 L.
Ferrous Chlorid, 63 Gm. to 1 L.
" *Sulphate
Gold Chlorid, 1 Gm. to 1 L.
Hydrogen Dioxid, 3%
Lead Acetate, 190 Gm. to 1 L.
" Nitrate, 165 Gm. to 1 L.
Lithium Chlorid, 4.3 Gm. to 1 L.
*Magnesia Mixture
Magnesium Sulphate, 61.5 Gm. to 1 L.
Manganese Chlorid, 31 Gm. to 1 L.
" Sulphate, 56 Gm. to 1 L.
Mercuric Chlorid, Sat. Sol.
Mercurous Nitrate, 70 Gm. to 1 L.
*Nessler's Reagent
Nickel Chlorid, 32 Gm. to 1 L.
" Sulphate, 70 Gm. to 1 L.
Potassium Acetate, 98 Gm. to 1 L.
" Aluminium Sulphate, 59 Gm. to 1 L.
" Bromid, 20 Gm. to 1 L.
" Carbonate, 207 Gm. to 1 L.
" Chlorate, 20.5 Gm. to 1 L.
" Chlorid, 37 Gm. to 1 L.
" Chromate, 97 Gm. to 1 L.
" Cyanid, 33 Gm. to 1 L.
" Dichromate, 49 Gm. to 1 L.
" Ferrocyanid, 105 Gm. to 1 L.
" Ferricyanid, 110 Gm. to 1 L.
" Fluorid, 58 Gm. to 1 L.
" Hydroxid, 140 Gm. to 1 L.
" Iodid, 17 Gm. to 1 L.
" Nitrate, 101 Gm. to 1 L.
" Nitrite, *fresh*, 250 Gm. to 1 L.
" Permanganate, 3.3 Gm. to 1 L.
" *Pyroantimoniate
Potassium Sodium Tartrate, 141 Gm. to 1 L.
" Sulphate, 44 Gm. to 1 L.
" Sulphid, 27.5 Gm. to 1 L.
" Thiocyanate, 97 Gm. to 1 L.
Silver Nitrate, 34 Gm. to 1 L.
Sodium Acetate, 136 Gm. to 1 L.
" Bicarbonate, 150 Gm. to 1 L.

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*See pages 21, 22.

Sodium Bitartrate, Sat. Sol.
" Carbonate, Sat. Sol.
" Chlorid, 29 Gm. to 1 L.
" Citrate, 98 Gm. to 1 L.
" *Cobaltic Nitrite
" Fluorid, 42 Gm. to 1 L.
(*Di*)" Hydrogen Arsenate, 104 Gm. to 1 L.
" Metarsenite, 130 Gm. to 1 L.
(*Di*)" Hydrogen Phosphate, 119 Gm. to 1 L.
" Hydroxid, 110 Gm. to 1 L.
" Hypochlorite, 37 Gm. to 1 L.
" Hypophosphite, 53 Gm. to 1 L.
" Metaphosphate, 102 Gm. to 1 L.
Sodium Pyrophosphate, 111.5 Gm. to 1 L.
" Silicate, Sat. Sol.
" Sulphate, 80.5 Gm. to 1 L.
" Sulphite, 63 Gm. to 1 L.
" Sulphid, 30 Gm. to 1 L.
" Thiosulphite, 124 Gm. to 1 L.
*Solution of Indigo
Solution of Litmus
Stannic Chlorid, 33 Gm. to 1 L.
*Stannous Chlorid
Starch Paste
Strontium Chlorid, 67 Gm. to 1 L.
" Nitrate, 53 Gm. to 1 L.
Zinc Chlorid, 31.5 Gm. to 1 L.
" Sulphate, 67 Gm. to 1 L.

SOLIDS

Acid Citric
" Oxalic
" Tartaric
Antimony Chlorid
Ammonium Aluminium Sulphate
" Chlorid
" Nitrate
" Oxalate
Barium Acetate
" Carbonate
" Chlorid
Bismuth Chlorid
" Nitrate
" Oxid (Bi_2O_3)
Borax
Cadmium Nitrate
" Sulphate
Calcium Chlorid
Chromium Chlorid
Cobalt Nitrate
" Sulphate
Copper Sulphate
" Foil, ¾ × ¾ inches
Ferric Chlorid
Ferrous Chlorid
" Sulphate, crystals
" Sulphid, coarse powder
Gold Chlorid
Lead Nitrate
Lead Oxid, (PbO)
Lithium Chlorid
Litmus Papers, Red and Blue
Magnesium Sulphate
Manganese Chlorid
" Dioxid
" Sulphate
Mercuric Chlorid
Mercurous Nitrate
Nickel Chlorid
" Sulphate
Platinic Chlorid
Potassium Aluminium Sulphate
" Bromid
" Chlorate, crystals
" Chromate
" Cyanid
" Dichromate
" Fluorid
" Iodid
" Nitrate
" Nitrite
" Sodium Tartrate
" Thiocyanate
Silver Nitrate
Sodium Acetate
" Bicarbonate

*See pages 22, 23.

Sodium Carbonate, dry
" Citrate
" Chlorid
" Dioxid
" Fluorid
(*Di*)" Hydrogen Arsenate
" Metarsenite
" Hypophosphite
" Metaphosphate
" Nitrate
" Nitroprussid
" Sulphite
" Thiosulphate

Stannic Chlorid
" Oxid
Stannous Chlorid
Strontium Chlorid
" Nitrate
Starch
Tumeric Papers
Zinc, granulated, *Arsenic-free*
" sheet, ½ × ½ inches
" Chlorid
" Oxid
" Sulphate

Chlorin Gas may be made by adding 18 parts of concentrated Hydrochloric Acid to 5 parts of Potassium Chlorate, just covered with a little water, and gently warming on a water-bath.

Hydrogen Sulphid Gas is made by adding diluted Sulphuric Acid to coarsely ground Ferrous Sulphid.

Chloroplatinic Acid may be made by covering 4.9 Gm. of clean metallic platinum with concentrated Hydrochloric Acid, and adding Nitric Acid in *very small portions* at a time, gently heating on a water-bath until dissolved. Any black residue should be filtered out, the liquid then evaporated to syrupy consistency, and finally enough Water added to make 100 Cc. (*mils*).

Ammonium Acetate Solution may be made by mixing equal volumes of 34.6% Acetic Acid and 10% Ammonium Hydroxid.

Ammonium Carbonate Solution is made by dissolving 195 Gm. of Ammonium Carbonate in 1000 Cc. (*mils*) of 10% Ammonium Hydroxid.

Ammonium Molybdate Solution is made by dissolving 75 Gm. of pure Ammonium Molybdate in 500 Cc. (*mils*) of Water; then pouring this solution into 500 Cc. (*mils*) of Nitric Acid (32.3%) and shaking until the precipitate dissolves.

Ammonium Sulphid, $(NH_4)_2S$, Solution may be made by passing Hydrogen Sulphid into 200 Cc. (*mils*) of 28% Ammonium Hydroxid, contained in a bottle which is immersed in running water or in ice water, until saturated; and then adding 200 Cc. (*mils*) more of the Ammonium Hydroxid and enough Water to make 1000 Cc. (*mils*).

AMMONIUM POLY-SULPHID, $(NH_4)_2S_x$, ("Yellow Ammonium Sulphid") Solution is made by digesting 1000 Cc. (*mils*) of Ammonium Sulphid, $(NH_4)_2S$, solution with 15 Gm. of powdered Sulphur for several hours, and then filtering.

FERROUS SULPHATE Solution may be made by dissolving 150 Gm. of crystalline Ferrous Sulphate in enough Water to make 1000 Cc. (*mils*), and adding a few clean scraps of Iron and 5 Cc. (*mils*) of concentrated Hydrochloric Acid.

MAGNESIA MIXTURE may be made as follows: Dissolve 100 Gm. of crystalline Magnesium Chlorid and 200 Gm. of Ammonium Chlorid in 1300 Cc. (*mils*) of Water. Dilute this solution to 2 L. with 10% Ammonium Hydroxid.

NESSLER'S REAGENT (Potassium Mercuric Iodid): Dissolve 115 Gm. of Mercuric Iodid and 80 Gm. of Potassium Iodid in enough Water to make 500 Cc. (*mils*). Add 500 Cc. (*mils*) of a 20% solution of Sodium Hydroxid and decant the clear liquid from any precipitate that may form upon standing. Keep the reagent in amber bottles in a dark place. For sensitive work both the Water and the salts used must be free from Ammonia.

POTASSIUM PYROANTIMONIATE Solution: Add 20 Gm. of the solid to about 950 Cc. (*mils*) of boiling Water. Boil for one minute until almost all of the salt is dissolved. Quickly cool, and add about 30 Cc. (*mils*) of 10% solution of Potassium Hydroxid. Filter and dilute to 1 L. The clear liquid should be decanted from any flocculent precipitate that may form upon standing. This reagent should be tested at frequent intervals with a known solution of a Sodium salt.

SODIUM COBALTIC NITRITE: Dissolve 100 Gm. of Sodium Nitrite is 300 Cc. (*mils*) of Water; add enough Acetic Acid to give the solution a slight acid reaction; and then add 10 Gm. of Cobalt Nitrate. Let the mixture stand for several hours. Then filter if necessary. This reagent should be made up in small quantities at a time as it decomposes rather readily.

SOLUTION OF INDIGO: To 5 parts of *fuming* Sulphuric Acid, contained in a beaker immersed in cold water, add *slowly* with constant stirring 1 part of finely powdered Indigo. Cover the beaker and let the mixture stand for several days.

Then pour the mixture into twenty times its volume of Water, stir, and finally filter.

STANNOUS CHLORID Solution may be made by either of the following methods:

(*a*) Dissolve 100 Gm. of the crystalline salt in 200 Cc. (*mils*) of concentrated Hydrochloric Acid and dilute to 1000 Cc. (*mils*).

(*b*) Dissolve 55 Gm. of metallic Tin in 225 Cc. (*mils*) of concentrated Hydrochloric Acid, and dilute to 1000 Cc. (*mils*).

Keep some granules of Tin in the bottle and stopper with a cork stopper.

STARCH PASTE: Rub 40 Gm. of soluble Starch to a thin paste with a little Water, and pour this mixture into 1000 Cc. (*mils*) of boiling Water. Boil for five minutes and strain if necessary.

4. The student learns that the deportments of substances with "REAGENTS" constitute "TESTS," which form the basis of practical chemical analysis. It is important that each beginner follow each step of the manipulations as shown by the instructor, and exercise care in the use of reagents. The quantity of a reagent used is very important, and in order to limit the volume of fluids handled, all operations should be carried out in test-tubes, small beakers, dishes, etc. Cleanliness, above all things, must be emphasized and practised if success is looked for.

5. QUALITATIVE ANALYSIS consists in the identification of a simple substance or the identification of the constituents of a complex substance. The field therefore is too broad for this elementary manual, and consequently the student's attention will be confined to the more common elements and compounds of special interest to the Medical, Dental and Pharmaceutical branches. Only a few of the compounds of carbon, and none of the rare metals and acids will be considered. The chemical reactions referred to above as "TESTS" generally take place with difficulty between solids, but, as a rule, very readily between solutions. Since the majority of the tests in this manual are tests on solutions, the latter are therefore most important.

6. A SOLUTION may be defined as a homogeneous mixture of two or more substances (gas and gas, gas and liquid, gas and solid, liquid and liquid, liquid and solid, or even solid and solid), which cannot be separated into its constituents by mechanical means without altering the physical state of one of the substances, and whose properties vary with the proportions of its constituents between certain limits. Solutions of solids in liquids, liquids in liquids, and gases in liquids are the most important.

A solid may be distributed through a liquid either by being *suspended* in the liquid, or by being dissolved in it (*solution*). In like manner a liquid may be suspended in the form of minute drops in another liquid, as in milk (*emulsion*), or it may be dissolved. Ordinarily it is a simple matter to distinguish between the two cases, for a substance which is *suspended* sooner or later separates or settles, while a substance that is *dissolved* does not. However, there are some exceptional cases in which the subdivision of the suspended substance is so minute as to make retention of the suspended substances by filter paper impossible (*colloidal solution*). If a liquid is opaque or opalescent, it is a case of suspension. If it is clear, homogeneous and transparent, it is a case of solution, in which the dissolved substance seems to have been so completely dispersed that the liquid cannot be distinguished by the eye from a pure substance.

There is no limit to the degree of dissipation which may be thus produced. For example, a small crystal of Potassium Permanganate ($KMnO_4$), which gives a deep purple colored solution in water, may be dissolved in 10 or 20 L. of water, and the purple tinge which it gives the liquid will be perfectly perceptible in every part of the solution. The fundamental characteristics of solutions then are: (1) absence of settling, (2) homogeneity, and (3) extremely minute subdivision of the dissolved substances.

It should be remembered that the term "solution" is not limited to solutions of solids in liquids; for observation has shown that agitation of any gas with water results in the solution of a large or small quantity of the gas. Palladium or Iron can be made to absorb Hydrogen gas, liquids are in some cases absorbed by solids, and homogeneous mixtures of solids with solids are possible. It may therefore be said that solutions of gases, liquids, and solids in solids, and solids, liquids and gases in liquids may be made.

It is customary to call the substance which, like water in most cases, forms the bulk of the solution the SOLVENT. For the substance which is dissolved the term SOLUTE is used. The amount of the substance which has been dissolved in a given quantity of a solvent determines the CONCENTRATION of the solution. Since there is a limit to the solubility of most substances, a solution is called SATURATED when the solvent has dissolved as much of the solute as it normally can dissolve. When this condition is attained by prolonged agitation of the solvent with the solute, the *maximum concentration* is reached, and this is called the SOLUBILITY of the substance in a given solvent. The term MOLAR SOLUTION is frequently employed and refers to a solution containing one MOLE (*gram-molecular weight*) of the solute in 1 L. of solution. Thus in the case of a molar solution of Sulphuric Acid ($H_2SO_4 = 98$), a liter of the solution would contain 98 Gm. of Sulphuric Acid.

Practically all of the solutions to be used and studied in carrying out the work described in this manual are solutions of *acids*, *bases* and *salts*, and a study of some of the characteristic properties of these compounds shown in aqueous solution is of utmost importance to the student.

The student has already learned that all acids contain Hydrogen, in aqueous solution (if soluble) they are sour in taste, turn blue litmus red, and that their Hydrogen is displacable by certain metals and has the properties of a radical. Many other compounds, like alcohol, sugar, etc., contain Hydrogen also, but they do not show all of these properties. Further, all salts are made up of two radicals, and the reversible double decompositions into which they enter with acids, bases and other salts, consist in exchanges of these radicals. Other compounds may include the same combination of atoms, but in their actions these groupings are frequently disregarded. Thus, Silver Nitrate ($AgNO_3$) and Sodium Chlorid (NaCl) exchange radicals completely, according to the following equation:

$$AgNO_3 + NaCl \rightarrow AgCl + HNO_3$$

However, Sodium Chlorid and Nitroglycerin ($C_3H_5(NO_3)_3$) do not interact at all. The latter is not a salt, although it contains the same proportion of Nitrogen to Oxygen as does any nitrate.

It is chiefly in *aqueous solution* that these special characteristic properties of acids, bases, and salts become apparent. In the absence of the solvent (water), their behavior is frequently quite different. For example, if Ammonium Carbonate and partially dehydrated Cupric Nitrate are mixed and heated, a violent interaction takes place. A cloud of gas and smoke is given off, which consists of Nitrogen Peroxid, NO_2; Carbon Dioxid, CO_2; Nitrous Oxid, N_2O, Water vapor, Nitrogen, and possibly other products; and a black or reddish residue remains, which contains Cupric Oxid and at times red Cuprous Oxid (Cu_2O). On the other hand, if the substances are dissolved in water before bringing them in contact, a very different interaction takes place. A pale green precipitate of Cupric Carbonate ($CuCO_3$) is formed which rapidly settles to the bottom, and evaporation of the supernatant liquid would yield Ammonium Nitrate (NH_4NO_3). Thus, by the latter method but two main products are formed, and the essential part (a basic Cupric Carbonate is really formed) of the action may be represented by the equation:

$$(NH_4)_2CO_3 + Cu(NO_3)_2 \rightarrow CuCO_3 + 2NH_4NO_3$$

A marked difference is noted in the interactions between the substances when in the dry state and when in solution. In the dry state heat is required and the molecules are completely disintegrated, the whole change being very complex. In the case of the solutions, no heat is required, certain groups of atoms which are called radicals are transferred from one state of combination to another, and the rearrangement takes place in a quiet orderly manner.

7. Other compounds, however, show no change in behavior when dissolved in water. For example, Sugar ($C_{12}H_{22}O_{11}$) is usually more readily acted upon in the absence of a solvent. Further, although there are other solvents which have the effect of water just described, the majority of solvents retard chemical changes if they affect them at all. Thus Iodin and Phosphorus unite spontaneously with a violent evolution of heat when these elements are brought in contact in the absence of a solvent. If they are dissolved in Carbon Disulphid (CS_2) and then mixed, the reaction is much more mild although the same compound is formed (Phosphorus Tri-iodid, PI_3). It is apparent that the decrease in concentration of the ingredients retarded the speed of the action in this case. That water and some other solvents have a specific tendency to increase the activity of certain classes of compounds, shows that a special explanation of the phenomenon must be found.

Observation, then, has shown that the peculiarity of acids, bases, and salts in *aqueous solution* is that each compound always splits in the same way. Thus, Cupric Nitrate ($Cu(NO_3)_2$) always gives changes which involve Cu and NO_3, and never interacts so as to use CuN_2 or CuO_2 and O_3 or NO_2 as the basis of exchange. In like manner the acids always offer Hydrogen in exchange, so that Sulphuric Acid (H_2SO_4) acts as if composed of 2H and SO_4, but never as if composed of H_2S or HSO and O_4 or HO_3. (The characteristic sour taste and effect on litmus seem to be properties of the readily separable Hydrogen, since they are shown by all acids.) As a result of these observations a list of the units of exchange, such as H, OH, SO_4, Cu, Na, Cl, I, as employed by the acids, bases and salts in their interactions can be made. The molecules of each of these classes of compounds contain at least two of these exchange units.

Three or four other characteristics of aqueous solutions of acids, bases and salts will be described before an explanation is offered.

8. (A) OSMOTIC PRESSURE.—The student has already learned that the particles of a dissolved substance exercise a pressure very similar to that exercised by the gases, and that this pressure is spoken of as *Osmotic Pressure*. Further, that osmotic pressure increases when a solution is warmed, and it gains $1/273$ of the value it had at 0° for every degree through which the temperature is raised. (Compare with Charles' Law for gases.) So, as in the case of gases, the molecules of a dissolved substance are looked upon as being distributed through the space occupied by the solvent, as being separate from one another, and as being in a state of independent motion. He has also learned that osmotic pressure is proportional to the concentration of the solution; that is, that it depends upon the degree of crowding of the molecules of the dissolved substance. (Compare with Boyle's Law.) One of Pfeffer's experiments will serve to illustrate this.

% Sugar	*Osmotic Pressure*
1	535 mm.
2	1016 mm.
4	2082 mm.
6	3075 mm.

And further, if the concentrations of different solutions which at the same temperature exhibit equal osmotic pressures are compared, it is found that they contain the same number of molecules of the dissolved substances in equal volumes. Thus, if one mole (74 Gm.) of Methyl Acetate ($CH_3C_2H_3O_2$), and one mole (342 Gm.) of Sugar ($C_{12}H_{22}O_{11}$) are dissolved in equal volumes of water (equal numbers of the molecules of the two compounds having thus been taken), it will be found that the osmotic pressures exhibited by the two solutions are equal.

9. However, if a comparison of a solution of Sugar and a *salt*, such as Potassium Chlorid (KCl), is carried out a striking difference is noted. Thus, if the gram-molecular weight of Sugar (342 Gm.) is dissolved in enough water to make 22.4 L. at 0° (760 mm.), it exhibits, at 0°, the ***normal*** osmotic pressure of one atmosphere. On the other hand, a solution of one molecular weight of Potassium Chlorid (74.5 Gm.) in the same volume of water exhibits an osmotic pressure of about 1.88 atmospheres at 0°. The same is found in the cases of the other salts, and the acids and bases; that is, these substances in solution exhibit abnormally high osmotic pressures.

10. (B) VAPOR TENSION.—This the student has learned is the tendency of liquids to pass into the vaporous condition. He will recall that increase in temperature of a liquid increases its Vapor Tension, and that the presence of a dissolved substance in a liquid always *lowers* the Vapor Tension of the liquid, and that the lowering of the Vapor Tension for a fixed quantity of the liquid is proportional to the quantity of dissolved substance. Further, that equal lowering of Vapor Tension will be produced by dissolving gram-molecular weights of two different substances in equal volumes of the same liquid. Thus, 10 Gm. of Sugar dissolved in a liter of Water will depress or lower the Vapor Tension of the Water twice as much as 5 Gm. of Sugar dissolved in the same volume of Water. And 342 Gm. of Sugar ($C_{12}H_{22}O_{11} - 342$) and 92 Gm. of Glycerin ($C_3H_5(OH)_3 - 92$) dissolved in equal volumes of Water exhibit equal lowering of Vapor Tension.

However, the acids, bases and salts are exceptions to these rules. Thus, if 58.5 Gm. of the salt, Sodium Chlorid ($NaCl - 58.5$), and 342 Gm. of Sugar ($C_{12}H_{22}O_{11} - 342$) are dissolved in equal volumes of Water, it would be found that instead of producing equal depression of the Vapor Tension, the depression exhibited by the Sodium Chlorid is much greater. So the acids, bases and salts in solution exhibit *abnormal depression* of Vapor Tension as well as exhibiting *abnormally high* Osmotic Pressures.

11. (C) FREEZING POINT.—That the Freezing Point of a solution is depressed in direct proportion to the weight of the dissolved substance in a given amount of a solvent, and that this depression is inversely proportional to the amount of solvent are facts already known to the student. Thus, if we double the concentration of a solution, the depression in the Freezing Point is doubled. He has also learned that equal numbers of molecules of different solutes in the same quantity of solvent exhibit equal depressions. Thus, a solution containing 342 Gm. of Sugar ($C_{12}H_{22}O_{11} - 342$) in 1000 Gm. of Water, and a solution containing 46 Gm. of Alcohol ($C_2H_5OH - 46$) in the same amount of Water, exhibit a depression below the Freezing Point of Water of 1.89° in each case. However, *acids, bases and salts* dissolved in Water are exceptions to the above rules. Thus, in Smith's experiments when 58.5 Gm. of Sodium Chlorid ($NaCl - 58.5$)

were dissolved in 2000 Gm. of Water, and 74 Gm. of Methyl Acetate ($CH_3C_2H_3O_2$ – 74) were dissolved in the same amount of Water, it was found that the Methyl Acetate solution exhibited a depression in the Freezing Point of 0.970° (about half the average molecular depression, since the solution contains only 0.5 moles of the solute per liter), whereas the salt solution exhibited a depression of 1.678°. So in addition to exhibiting *abnormal depression of Vapor Tension* and *abnormal increase in Osmotic Pressure*, solutions of *acids*, *bases* and *salts* in aqueous solution exhibit *abnormal depression of the Freezing Point.* However, these substances when dissolved in such solvents as Carbon Disulphid (CS_2), Chloroform ($CHCl_3$), etc., simply exhibit *normal depressions.* It is apparent, therefore, that there is some decided difference in the condition of these substances when dissolved in water.

12. (D) BOILING POINT.—The Boiling Point, the student has learned, is *raised* when a substance is dissolved in a solvent. Thus, if the solvent is Water, one mole of a solute in 1000 Gm. of the solvent *normally* raises the Boiling Point 0.52°; that is, from 100° to 100.52°. But here again, *acids*, *bases* and *salts* form an exception to the rule by exhibiting an *excessive* or abnormal increase in the Boiling Point.

13. IONIZATION.—What explanation can be offered of the above facts? "Ionization" or "Dissociation in Solution" is the answer. For the above described peculiarities in the *chemical behavior*, the *osmotic pressures*, the *vapor tensions*, the *freezing points*, and the *boiling points* of solutions of ACIDS, BASES, and SALTS constitute proofs that these substances when in aqueous solution are actually DISSOCIATED INTO PARTS BY THE SOLVENT. These parts, it will be seen, coincide in composition with the radicals and are called IONS.

Let the experiment described in ¶9 be considered from the standpoint of *Dissociation* or *Ionization*. Two solutions, each containing the same number of molecules of two different substances, Sugar and Potassium Chloride, in the same volumes of Water were examined. The Sugar solution exhibited the *normal osmotic pressure* of one atmosphere at 0°, whereas the Potassium Chlorid solution exhibited an osmotic pressure of about 1.88 atmospheres at 0°. This greater pressure then must be due to the fact that although the number of *molecules* of Potassium Chlorid taken was the same as the number of molecules of Sugar, the number of ACTUAL PARTICLES whose impact constituted the pressure is GREATER. In the case of Potassium Chlorid the number must be about 88% greater (one atmosphere as compared to 1.88 atmospheres). But the multiplication of particles from Potassium Chlorid molecules can occur only by the dissociation or breaking up of the molecules into particles of Potassium (K) and of Chlorin (Cl), as represented by the following equation:

$$KCl \rightleftarrows K + Cl^{*}$$

Thus, in the solution of Potassium Chlorid the pressure exhibited is due to the impact of the particles (IONS) of Potassium and the particles (IONS) of Chlorin, instead of to the molecules (KCl); and, if all of the molecules of the salt were dissociated, the osmotic pressure exhibited would have been 2 atmospheres instead of 1.88, since each molecule of KCl would yield one particle (ION) of Potassium and one particle (ION) of Chlorin. It therefore follows that 0.88 (1.88 − 1.00) or 88% of the molecules of Potassium Chlorid must have been broken up into ions. Experiments have shown that the degree of dissociation of different acids, bases and salts varies widely, and that for the same substance it is always relatively greater in dilute than in concentrated solutions.

In like manner can be explained the abnormal depression of the freezing point described in ¶11(C). It was seen that the Methyl Acetate solution exhibited normal depression, while the salt solution, NaCl, exhibited abnormal depression; that is, the freezing point of the salt solution was much lower. Since equal numbers of molecules of different solutes in the same quantity of a solvent should exhibit equal depression, and aqueous solutions of acids, bases and salts exhibit a greater depression, it follows that in the cases of aqueous solutions of these substances, their molecules must undergo dissociation whereby a greater number of particles are present. Thus, in the case of the Sodium Chlorid (NaCl) solution, dissociation results in the presence of particles or ions of Sodium and ions of Chlorin, and instead of having simply molecules (NaCl) of Sodium Chlorid, there are present the ions of Sodium and the ions of Chlorin; that is, two ions for every molecule which undergoes dissociation. Here also the excessive depression varies with the acid, base or salt involved, and is dependent upon the degree of dissociation of the substance. Experiments indicate that the more dilute the solution, the greater the degree of dissociation or ionization, within certain limits. In the case of a salt like Calcium Chlorid, $CaCl_2$, the depression would be about three times the normal value, since its molecules would give three ions in solution (Ca, Cl, Cl).

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* The ⇄ indicates that the action is "reversible." Reversible actions are explained on pages 43–45, ¶ 21.

If space permitted, statements might be made in regard to the vapor tensions and the boiling points of solutions which would be closely parallel to those already made about osmotic pressure and freezing points in which it would be shown that the abnormal depression of the vapor tensions and the excessive increase in boiling points exhibited by the solutions of acids, bases and salts are due to the dissociation of the molecules of these substances and measured by the degree of such dissociation.

14. From the above then it appears that Water (and some other solvents like Alcohol, C_2H_5OH) has the power of breaking up the molecules of acids, bases and salts and of holding the resulting particles or ions apart from one another and preventing them from reuniting. Therefore, an aqueous solution of an acid, such as Hydrochloric Acid, HCl, or a base, such as Sodium Hydroxid, NaOH, or a salt, such as Sodium Chlorid, NaCl, contains, besides undivided molecules of the solute, at least two other kinds of material, H, Na, OH, Cl, etc., which result from the dissociation of the molecules. However, it must be noted that these subdivisions of the original molecules have distinctive properties, physical and chemical, of their own. Thus the Hydrogen ion of acids, although a form of uncombined Hydrogen, differs totally from gaseous Hydrogen. Gaseous Hydrogen has no sour taste, has no effect on litmus, and is only very

PREFACE TO SECOND EDITION.

THE kindly reception accorded the first edition of this laboratory manual makes this second edition necessary to fill the wants of the numerous colleges and schools which have adopted the manual. It is also gratifying to note that the National Association of Dental Faculties through its text-book committee has recommended this manual as the required text for laboratory instruction in Qualitative Analysis.

This edition has been completely and thoroughly revised, and the author feels confident that the changes, corrections, and additions made will be helpful to the beginner in analytical chemistry. The lists of compounds and preparations which followed each cation and anion, and the blank pages for the writing of equations have been eliminated in this edition in order to make the manual more compact and to bring the various parts of the book closer together, a very desirable feature for any cross reference book. The introduction has been enlarged, the old "Group 4" of the cations has been split into two smaller groups, a separate chapter on the analysis of an unknown added, insoluble substances considered, the analysis of metals and alloys included, and a table of solubilities added. These in addition to numerous less important changes and additions.

The author desires to express his grateful appreciation for many valuable criticisms and suggestions offered by his colleagues, particularly Doctor Henry J. Goeckel, formerly of the Chemical Department of New York University, now biological chemist and pathologist to the Muhlenberg Hospital, Plainfield, N. J. The author is also very grateful to his wife for her careful assistance in the revision of the manuscript and the index.

A. R. BLISS, JR.

ATLANTA, GA.
April, 1918.

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slightly soluble in Water, while the Hydrogen ion of acids has a sour taste, turns blue litmus red, and exists as a separate substance only in solution. Further, substances with the composition of the ions SO_4 or NO_3 are not known except in solutions. A striking peculiarity of these substances however, is that a solution cannot be made which contains less than two kinds of ions.

An ION, then, may be defined as an atom or a group of atoms formed through the dissociation of an acid, a base or a salt by a solvent like Water. And further their composition corresponds to that of the radicals. The term "IONIZATION" may be defined as the dissociation of molecules into ions; and the substances of the three classes which alone are ionized may be called IONOGENS.

Since the ions are chemically different from their parent molecules, their formation represents a variety of chemical change which is simply a reversible decomposition of the dissolved substance. We know that this is a reversible action* and a true dissociation because of the following fact already called to the student's attention: the proportion of the molecules ionized becomes greater as more of the solvent is added; and because of the fact that removal of the solvent diminishes the proportion of the ions to molecules, and finally leaves the substance entirely restored to molecular condition. (Thus, if a solution of Sodium Chlorid (NaCl) is made and then evaporated, the original substance in its original state is obtained.) In the cases mentioned in ¶14 the following equations represent the actions taking place:

$$\begin{aligned} HCl &\leftrightarrows H^+ + Cl^- \\ NaOH &\leftrightarrows Na^+ + OH^- \\ NaCl &\leftrightarrows Na^+ + Cl^- \end{aligned}$$

In these equations the symbols H^+, Cl^-, OH^-, etc., are used to indicate that they are ions, and not identical with atoms, H, Cl, etc. The positive ions or radicals are distinguished by the plus sign thus, Na^+, Mg^{++}, and the negative by the minus sign, Cl^-, SO_4^{--}. The reason for this marking will be explained presently.

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* See ¶ 21, page 43.

15. ELECTROLYSIS.—In taking up this topic the student *must* keep in mind the fact that Electrolysis *does not produce* ionization. The electrolytic property of the ions which will be described here is only one of the many special properties of ionogens, the majority of which are chemical and have nothing to do with electrolysis. Unless this fact is kept in mind, the student is likely to be greatly confused and handicapped in his work.

Experiment shows that most solutions which exhibit chemical transformations by the interchange of groups, and which exhibit the property of dissociation (as shown by the *abnormal* effects on osmotic pressure, vapor tension, and the boiling and freezing points), are the same solutions which will conduct electricity and undergo decomposition by the passage of the electric current through them. On the other hand, solutions which have the *normal* effect on the four physical properties mentioned above; that is, solutions which do not dissociate, are non-conductors. The term "ELECTROLYTE" is employed to designate a solution which will conduct the electric current and undergo decomposition by its passage; and often this term is applied to acids, bases and salts, themselves, because when dissolved they produce "electrolytes." The employment of the term in the latter fashion, however, is likely to lead to confusion, since these compounds by themselves are *not conductors*. The term "ELECTROLYSIS" is used to designate the effect of an electric current upon electrolytes. Solutions of Sugar, Methyl Acetate, etc., are non-conductors, and it has already been shown that they are undissociated. Solutions of acids, bases or salts in Chloroform, Toluene, etc., do not conduct the electric current, neither do they show any evidence of ionization.

It must be remembered that the pure solvent itself and the pure solute which is dissolved in the solvent by itself are, at ordinary temperatures, almost complete non-conductors. Pure Water, dry Hydrochloric Acid, and dry Salts, except when at a high temperature and fused, do not permit the passage of the current. Yet a mixture of the Water with one of the others gives a solution which conducts the current very well. The nature of the decomposition which accompanies the conduction of the current must therefore be considered.

When the wires from a battery are attached to Platinum plates and the plates immersed in an electrolyte, it is noticed that products appear at the two plates (electrodes) and that these products are always different. They may be collected and examined according to their physical and chemical properties. If the products are gases which are not very soluble, they may be collected in inverted tubes which are filled with the solution. If they are solids, insoluble in the liquid, they will remain attached to the plates or be present as precipitates in the bottom of the container. If the products are soluble substances, they will usually be invisible.

16. A typical example that will serve to illustrate this phenomenon is Silver Nitrate, $AgNO_3$. If an electric current is passed through an aqueous solution of this salt, it will be noticed that metallic Silver is liberated at the negative plate or electrode and adheres to it; while at the positive electrode Oxygen gas is liberated. However, these products account for but two of the three elements that compose Silver Nitrate. If the liquid found around the positive electrode is examined, it will be found that Nitric Acid (HNO_3) is being liberated along with the Oxygen. It is true that a third part is found, but it is something more than the element Nitrogen, the third element of the salt $AgNO_3$. This, however, is easily explained for a solution of a salt, like Silver Nitrate, contains two kinds of ions which result from the division of the molecules of $AgNO_3$; namely Ag and NO_3. The NO_3 is not a known compound, and therefore must have interacted with the Water thus:

$$2NO_3 + H_2O \rightarrow 2HNO_3 + O$$

The atomic Oxygen must have united so as to form gaseous Oxygen, O_2. Therefore the entire change may be expressed as follows:

− **Electrode:** $Ag \leftarrow Ag.NO_3 \rightarrow O_2$ and HNO_3: + **Electrode**

If a solution of Potassium Nitrate (KNO_3) is used, Hydrogen would appear at the negative electrode, and Oxygen at the positive. At the negative plate, however, would be found also the base Potassium Hydroxid, KOH; and at the positive an acid, Nitric Acid, HNO_3. It is assumed then that the parts or ions of the parent molecules, KNO_3, are K and NO_3. The Potassium reacts with the Water giving rise to free Hydrogen and Potassium Hydroxid, instead of being liberated itself, according to the following equation:

$$2K + 2H_2O \rightarrow 2KOH + H_2$$

The NO_3, of course, would conduct itself as already described above. Thus, the whole change may be represented as follows:

$$-\textbf{ Electrode: } H_2 \text{ and } KOH \leftarrow K.NO_3 \rightarrow O_2 \text{ and } HNO_3 : +\textbf{ Electrode}$$

If an acid, like diluted Sulphuric Acid, H_2SO_4, is subjected to electrolysis, Hydrogen is liberated at the negative electrode, Oxygen is liberated at the positive, and there is also an accumulation of Sulphuric Acid around the positive electrode; thus:

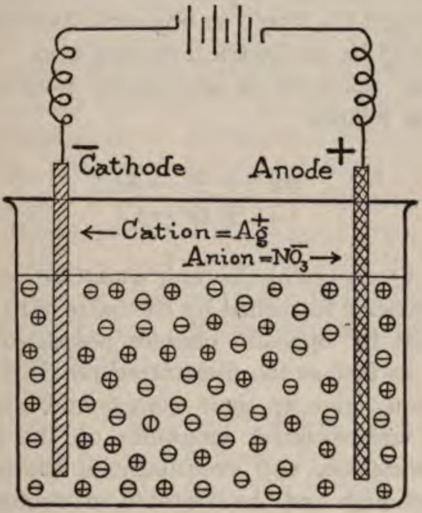
$$-\textbf{ Electrode: } H_2 \leftarrow H_2.SO_4 \rightarrow O_2 \text{ and } H_2SO_4 : +\textbf{ Electrode}$$

It is found that all acids give Hydrogen alone at the negative electrode, and the salts are divided into their radicals by the electric current.

The question arises why are the parts into which the molecules of acids, bases and salts divide upon entering into a state of solution attracted by the electrically charged electrodes when these are immersed in the solution, when molecules of other substances in solution, such as Sugar, are not attracted? The answer is rather simple. Observation has shown that the only bodies which are decidedly attracted by electrically charged objects are those which already possess electric charges of their own. Therefore, it must be true that when substances which dissociate in solution are dissolved, their molecules *divide themselves into special electrically charged atoms or molecules*, and, since the solution, as a whole, has no charge itself, equal quantities of positive and of negative electricity must be produced; thus:

$$\begin{aligned} HCl &\rightarrow H^+ + Cl^- \\ NaOH &\rightarrow Na^+ + OH^- \\ NaCl &\rightarrow Na^+ + Cl^- \end{aligned}$$

The following diagram will assist the student in studying this phenomenon. It represents a vessel containing a solution of Silver Nitrate, $AgNO_3$, into which have been introduced the electrodes of a battery. The student has already learned that upon entering a state of solution Silver Nitrate, being a salt, undergoes Dissociation or Ionization, which results in the presence of two kinds of ions in the solution; namely, Ag ions and NO_3 ions. Upon the introduction of the electrodes, the negatively charged one (*cathode*) attracts all the positively charged particles which begin to drift toward this plate and these are called "CATIONS." Since the Silver is deposited on this electrode, it follows that the Silver particles must have been attracted by this electrode and must possess positive charges, and are therefore the "cations" of this solution. On the other hand, the



negatively charged particles, the NO_3, are repelled by this electrode and are attracted by the positive electrode (*anode*) toward which they drift. The negatively charged particles or ions are called "ANIONS." In each case those particles or ions which are nearest the electrodes on coming in contact with the plates lose their charges of electricity and are turned into the free or ordinary forms of the matter of which they are composed. This continuous removal of electrical charges from the electrodes or plates through contact with ions possessing opposite charges requires the recharging of the plates from the battery, thus giving rise to a continuous current in each electrode. The drifting of positively and negatively charged particles through the liquid in opposite directions constitutes what appears to be an electrical current also. The liberation of ions at an electrode in electrolysis may be graphically represented as follows:

$$Ag^+ + \ominus \rightarrow Ag$$
$$Cl^- + \oplus \rightarrow Cl$$

The $\oplus$ and $\ominus$ represent the unit quantities of positive and negative electricity furnished by the battery to the electrodes and destroyed by opposite charges possessed by the ions. In this way as fast as the dissociated portions of the solute, that is, the ions, give up their charges and become free substance, the undissociated molecules of the solute present undergo dissociation, and eventually, if the process is continued long enough and the liberated substances are actually deposited and do not go into solution again in any form, the liquid is entirely freed from the solute which it contained.

The student is possibly troubled with the question "How can an element like Potassium exist in atomic condition in Water without acting upon it?" It must be remembered that the ions of Potassium in, for example, a solution of Potassium Chlorid, KCl, are *not metallic* Potassium. "How do they differ?" They carry large charges of electricity and possess an entirely different and much smaller amount of chemical energy than free or metallic Potassium. These facts have been demonstrated again and again by experiments in which actual measurements were made. The student has already learned that the properties of a substance are determined as much by the energy it contains as by the kind of matter. It follows then, that *ionic* Potassium and *metallic* Potassium are simply different substances.

17. THE AMOUNT OF IONIC ELECTRIC CHARGES.—If the electrolysis of Hydrochloric Acid is carried out, it is found that one atomic weight of Hydrogen (1.008) and one atomic weight of Chlorin (35.45) are liberated simultaneously. That is, there would be 1.008 parts of Hydrogen liberated and 35.45 parts of Chlorin. Since the solution remains electrically neutral, it follows that the ions of Hydrogen and the ions of Chlorin bear equal charges. And, since the same thing is true for a solution of Cupric Chlorid, one atomic weight of Copper (63.6 parts) and *two* atom weights of Chlorin (70.9 parts) being liberated, it follows that the Cupric ion possesses a double charge. Similarly, the Bismuth ions possess triple charges. It may therefore be stated that *ions possses electrical charges in direct proportion to their valences.*

In writing equations involving charges, the numbers of charges, positive and negative, may be designated by placing the signs + and − to the upper right side of the symbol or formula, and the numbers of + and − charges must always be equal:

$$HCl \rightleftarrows H^{+} + Cl^{-}$$
$$CuCl_2 \rightleftarrows Cu^{++} + 2Cl^{-}$$
$$BiCl_3 \rightleftarrows Bi^{+++} + 3Cl^{-}$$

18. To summarize then, the following points are important:

1. An ION is an atom or group of atoms which bears a positive or negative electrical charge, and is formed through the dissociation of an ionogen by a solvent like Water.
2. Each molecule of ionogens gives two kinds of ions which possess opposite charges, and which differ from non-ionic substances of the same material when such are known.
3. The electrical charge possessed by an ion is one of its essential constituents, and when it is removed, the properties alter entirely. Thus, there are two kinds of

Hydrogen: (*a*) gaseous or molecular Hydrogen, H_2; and (*b*) ionic Hydrogen, H^+, with different chemical properties.

4. Ions which proceed in the same direction as the positive current are called CATIONS. Examples are: H^+, Na^+, Bi^{+++}, Cu^{++}, NH_4^+. They are metallic elements, or groups which conduct themselves like metals. The electrode which attracts them or upon which they are deposited, the negative electrode, is called the CATHODE.

5. Ions which move in the direction of the negative current are called ANIONS. They are usually non-metals, such as Cl^-, Br^-, NO_3^-, SO_4^{--}, although at times the components may be partially metallic as in the anion MnO_4^-. They are attracted to the positive electrode which is called the ANODE.

6. In equations involving charges, the numbers of + and − charges must always be equal.

7. Ionization or Dissociation in Solution is NOT produced by Electrolysis.

8. Ions possess electrical charges in direct proportion to their valences. Thus, univalent elements, like Hydrogen and Chlorin, possess the same quantity of electricity: H^+ and Cl^-; Magnesium which is divalent, Mg^{++}; Bismuth which is trivalent, Bi^{+++}; etc.

19. Since ionic Hydrogen, Chlorin, etc. are entirely different in physical and chemical properties from the corresponding free or ordinary elements, special names have been given the ions. The following is a partial list. After becoming familiar with these, the student will have no difficulty in assigning names to the other ions as he comes to them.

NAME	SYMBOL	CATION OF SALTS OF
Hydrion	H^+	Hydrogen (acids)
Natrion	Na^+	Sodium
Kalion	K^+	Potassium
Calcion	Ca^{++}	Calcium
Diferrion	Fe^{++}	Ferrous Iron
Triferrion	Fe^{+++}	Ferric Iron
Dicuprion	Cu^{++}	Cupric Copper
Ammonion	NH_4^+	Ammonium

NAME	SYMBOL	ANION OF
Hydroxidion	OH^-	Hydroxids (bases)
Chloridion	Cl^-	Chlorids
Bromidion	Br^-	Bromids
Chloranion	ClO_3^-	Chlorates
Sulphidion	S^{--}	Sulphids
Sulphanion	SO_4^{--}	Sulphates
Sulphosion	SO_3^{--}	Sulphites
Nitranion	NO_3^-	Nitrates

From now on the student must no longer look upon solutions of acids, bases and salts as solutions containing but one substance beside Water. He must think of them now as containing at least three dissolved substances, any one of which might be alone responsible for some property of the solution. He should further remember that the degree of ionization or dissociation is dependent on the substance dissolved and the concentration of the solution. Thus, when 0.1 molar solutions (0.1 of the gram-molecular weight in 1 L.) of Nitric (HNO_3), Hydrochloric (HCl), Sulphuric (H_2SO_4), Acetic ($HC_2H_3O_2$), Carbonic (H_2CO_3), Sulphydric (H_2S), and Boric (H_3BO_3) are compared the following percentages of each are dissociated:

HNO_3	90%
HCl	90%
H_2SO_4	60%
$HC_2H_3O_2$	1.5%
H_2CO_3	0.2%
H_2S	0.1%
H_3BO_3	0.01%

Therefore the strength of an acid is dependent upon its degree of dissociation, or in other words its capacity to furnish Hydrion (H^+). Thus, Nitric Acid is stronger than Sulphuric and many times stronger than Acetic, Carbonic, Sulphydric and Boric Acids. In the cases of 0.1 molar solutions of the bases, Potassium Hydroxid (KOH), which furnished in solution Kalion (K^+) and Hydroxidion (OH^-); Sodium Hydroxid ($NaOH$), which gives Natrion (Na^+) and

Hydroxidion (OH^-); Barium Hydroxid, which gives Barion (Ba^{++}) and Hydroxidion ($OH^- + OH^-$); and Ammonium Hydroxid (NH_4OH), which gives Ammonion (NH_4^+) and Hydroxidion (OH^-); the percentages of dissociation are as follows:

KOH	90%
NaOH	90%
$Ba(OH)_2$	75%
NH_4OH	1.5%

So the strength of the bases is also dependent on the degree of dissociation, or in other words on the capacity to furnish Hydroxidion (OH^-).

In the cases of the salts the percentages of dissociation are about as follows:

Type B^+A^-, like $NaNO_3$	84%
Type $B_2^+A^{--}$ or $B^{++}A_2^-$, like Na_2SO_4 or $BaCl_2$	73%
Type $B_3^+A^{---}$ or $B^{+++}A_3^-$, like $K_3Fe(CN)_6$ or $AlCl_3$	65%
Type $B^{++}A^{--}$, like $MgSO_4$	65%

20. Neutralization.—When an acid reacts with a base the Hydrion, H^+, combines with the Hydroxidion, OH^-, forming Water, H_2O. This process is called NEUTRALIZATION. The remaining cation combines with the remaining anion and forms a substance called a Salt. The action between Potassium Hydroxid, KOH, and Hydrochloric Acid, HCl, is represented as follows:

$$KOH + HCl \rightleftarrows KCl + H_2O$$

or

$$K^+ + OH^- + H^+ + Cl^- \rightleftarrows K^+ + Cl^- + H^+ + OH^-$$

Certain Hydroxids such as Zinc Hydroxid, $Zn(OH)_2$, and Lead Hydroxid, $Pb(OH)_2$, may be looked upon as bases or acids depending on what actions are involved. They may act as weak bases giving Hydroxidion, OH^-, and neutralizing an acid forming salts; or they may act as weak acids giving hydrion, H^+, and neutralizing a base. As acids they are written H_2ZnO_2 and H_2PbO_2, and, reacting with a base like Sodium Hydroxid, NaOH, form the soluble salts Na_2ZnO_2

and Na_2PbO_2. As bases they can neutralize an acid like Nitric Acid forming the soluble salts $Zn(NO_3)_2$ and $Pb(NO_3)_2$. Substances which are capable of acting either as an acid or a base are termed AMPHOTERIC.

It must also be remembered that in most of the solutions the student will use in the following work the great part and the most active part of the contents is almost always *ionic*, and the reactions to be studied take place mostly between the ions. Further that each kind of ion in a solution acts in many ways as if it were present alone, and has its individual physical and chemical properties. Thus, if aqueous solutions of different permanganates, such as Potassium Permanganate, $KMnO_4$, Sodium Permanganate, $NaMnO_4$, and Barium Permanganate, $Ba(MnO_4)_2$, were made one might expect to have solutions possessing decidedly different shades of purple. But if diluted solutions of these substances are made having equivalent concentrations, it would be found that the three solutions have the identical tint. Therefore, the three different solutions compared all contained the same proportion of the same free, colored ion, MnO_4^-. As has already been stated in the cases of solutions of acids, the sour taste is characteristic of all of them irrespective of the nature of the negative ion. However, salts which contain the same negative ion as the acids may not be in the least sour. Therefore, in the cases of the acids, the free substance, Hydrion, H^+, imparts the sour taste. In like manner, the soapy taste of the substance Hydroxidion, OH^-, in solutions of alkalies is noted.

21. REVERSIBLE ACTIONS.—In the equations on pages 31–42 the student has undoubtedly noted the use of the "double arrow," $\rightleftarrows$. Where this is used it indicates that the action is "REVERSIBLE." However, this does *not* mean that the action is one that goes to completion, and then runs back to a certain extent, for this would be contrary to fact. By a REVERSIBLE ACTION is meant one which can be made to proceed in one direction, forming new substances, or backward, *reforming* the original substances, by altering the temperature, the pressure, or the concentrations of one or more of the original substances or the new products formed.

At one time it was thought that this kind of action was rare, but now all chemical actions are looked upon as being reversible ones, although in many cases and especially in most of the actions used in chemical analysis, the action goes so completely in one direction that only a negligible quantity of one or more of the original substances remains unchanged. The precipitation of Zinc Sulphid, ZnS, from Zinc Chlorid, $ZnCl_2$, solution by Hydrogen Sulphid, H_2S, as expressed in the following equation, is an excellent example of a reversible action:

$$ZnCl_2 + H_2S \rightleftarrows ZnS + 2HCl$$

If the precipitated Zinc Sulphid is filtered off and treated with Hydrochloric Acid it will dissolve, as expressed in the equation reading from right to left. It is therefore evident that there are two opposing tendencies—(*a*) the tendency of the Zinc Sulphid to precipitate; and (*b*) the tendency of the Zinc Sulphid to dissolve. In carrying out the above action if the theoretical amount of Hydrogen Sulphid required to combine with the amount of Zinc present was taken, it is true that a precipitate of Zinc Sulphid would be obtained, but actual determination would show that *not all* of the Zinc would be precipitated from solution. The Hydrochloric Acid as it forms has a tendency to dissolve the Zinc Sulphid, thus stopping the precipitation before completion. That is, an equilibrium has been established in the solution.

Another excellent illustration of this kind of action is the formation of the soluble *blood-red* Ferric Thiocyanate ($Fe(CNS)_3$) by adding a solution of Ammonium Thiocyanate, NH_4CNS, to a solution of Ferric Chlorid, $FeCl_3$. The equation is as follows:

$$FeCl_3 + 3NH_4CNS \rightleftarrows Fe(CNS)_3 + 3NH_4Cl$$

If these salts are mixed in very dilute solutions in the proportions required by the equation, a pale-reddish solution is obtained. If this mixture is divided into four parts, and one kept for comparison, the addition of a small quantity of a concentrated solution of Ferric Chlorid to one of the other portions will result in a deepening of the color, due to the formation of more Ferric Thiocyanate. If a small amount of a concentrated solution of Ammonium Thiocyanate is added to the third portion, a similar deepening of the color will be noted for the same reason. On the other hand, if a few drops of a concentrated solution of Ammonium Chlorid are added to the fourth portion, it will be noted that the color almost entirely disappears on account of its influence in accelerating the backward action.

22. MASS ACTION.—The facts stated in the preceding two paragraphs are summarized in the law known as "THE LAW OF MASS ACTION," which states that THE SPEED AND ALSO THE AMOUNT OF A CHEMICAL ACTION IS PROPORTIONAL TO THE MOLECULAR CONCENTRATION* OF EACH INGREDIENT. In the case of the action between the Zinc Chlorid and the Hydrogen Sulphid, the law of mass action applied only to the Zinc Sulphid that remained in solution. The fact that this substance is only very slightly soluble in Water favors the progress of the action in the direction by which it was formed. The law of mass action shows that (*a*) when the concentration of any substance that takes part in a chemical action is increased, this tends to increase the tendency for the action to take place in the direction by which this substance was decomposed; (*b*) when any substance formed by a chemical action is removed, this tends to increase the tendency for the action to proceed in the direction by which this substance is formed. Thus, in the case of the Zinc Chlorid and the Hydrogen Sulphid, the formation of the precipitate, ZnS, tends to make the action take place more completely, and, if the precipitate were absolutely insoluble in Water, the action by which this substance is formed *would* take place completely. In the case of the mixture of Ferric Chlorid and Ammonium Thiocyanate solutions, the addition of a small amount of Ferric Chlorid or of a small amount of Ammonium Thiocyanate increased the concentrations of these substances and therefore the action proceeded in the direction whereby these substances were decomposed, with the result that more Ferric Thiocyanate is formed as shown by the deepening of the color. The addition of the Ammonium Chlorid, on the other hand, increased the concentration of this substance and the action took place in the backward direction as shown by the disappearance of the color.

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* Some authors employ the term "*active mass*" instead of "*molecular concentration*," but this is likely to be misleading to the student, for it is not the mass of the substance, but the quantity of it in a given volume on which the speed and the amount of a chemical action depends.

This law of mass action constitutes one of the most important principles utilized in analytical chemistry. It enables the worker to understand why most of the chemical actions take place and to establish the conditions under which the actions will take place to the best advantage.

In general then, when two substances, A and B, react with one another at a constant temperature to form the new substances C and D, to some extent at least the new substances formed, C and D, react to reform substances A and B, the original substances; and equilibrium is reached when the ratio of the product of the concentrations of substances A and B to the product of the concentrations of C and D has a definite, constant value, which value is characteristic of the equilibrium between the substances involved. The action may be expressed as follows:

$$A + B \rightleftarrows C + D$$

If A, B, C, and D represent the four different substances reacting in the molecular proportions indicated by their symbols; a, b, c, and d the molecular concentrations of the four reacting substances; and x the amount of A and B changed at any given time; then

$$R \text{ (the rate) } = K \cdot a \cdot b, \text{ when } x = 0 \text{ at the beginning,}$$

but

$$R = K\,(a - x)\,(b - x) \text{ afterward,}$$

in which cases K is a constant, called the equilibrium constant. It varies with the temperature. In the same equation, at the *beginning of the reverse action*

$$R' \text{ (the rate) } = K' \cdot c \cdot d$$

and at any time afterward

$$R' = K'\,(c + x)\,(d + x).$$

As the action proceeds a time must come when the rate of the forward action and the rate of the reversed action are equal; that is, $R = R'$, and then

$$K(a - x)(b - x) = K'(c + x)(d + x)$$

or

$$\frac{(a - x)(b - x)}{(c + x)(d + x)} = \frac{K'}{K}.$$

This, then, is the condition that exists when equilibrium is reached, at which point the product of the molecular concentrations of the original substances divided by the product of the molecular concentrations of the new substances formed is a constant.

Many applications of this law are made in analytical chemistry. All cases of ionization may be considered reversible actions in which the molecules dissociate into ions, which again combine to form molecules under given conditions of temperature and pressure until there is as much dissociation as combination; that is, equilibrium exists. For example Potassium Chlorid, KCl, dissociates according to the following equation:

$$KCl \rightleftarrows K^+ + Cl^-$$

If c is the molecular concentration of Potassium Chlorid, KCl; a, the *ionic* concentration of the Potassium ions, K^+; and b, the *ionic* concentration of the Chlorin ions, Cl^-; then the rate of dissociation of the Potassium Chlorid is

$$R = Kc.$$

And the rate of combination of the ions is

$$R' = K'ab.$$

When equilibrium exists; that is, when $R = R'$, then

$$Kc = K'ab$$

or

$\frac{ab}{c} = \frac{K'}{K}$ = a constant, called the *ionization constant.*

23. Solubility Product.—When a substance is precipitated from a solution it is assumed that there remains in solution as much of the substance precipitated as the liquid can keep in solution in the presence of the solid precipitated; that is, the liquid really is a saturated solution of the precipitated substance. For the case of a saturated solution the value of c in the equation $\frac{a \cdot b}{c} = K$ becomes constant and may be incorporated with K, so that

$$a \cdot b = Kc = K'.$$

a and b represent the amount of ions in the saturated solution and their product is called the SOLUBILITY PRODUCT. Disturbing this product by the addition of some substance in solution which contains one of the ions, results in an increase in a or b, and therefore a or b will be decreased and more undissociated molecules will be formed, and more of the substance will be precipitated because the solution is already saturated with the undissociated molecules. Thus, if Lead Sulphate, $PbSO_4$, is precipitated from a solution, the addition of a slight excess of a sulphate solution or Sulphuric Acid will result in an increase in the amount of Lead Sulphate precipitated, for the saturated solution of Lead Sulphate left after the first addition of the precipitant contains Pb^{++} and SO_4^{--} ions in such quantities that $a \cdot b$ = a constant. (a represents the amount of Pb^{++} ions, and b represents the amount of SO_4^{--} ions.) When a solution of a sulphate or of Sulphuric Acid is added, an excess of b (SO_4^{--}) results, and therefore a (Pb^{++}) must diminish in order to preserve the truth of the equation $a \cdot b = K$. The only possible way for this to take place is by the formation of more undissociated Lead Sulphate; and, since the solution is saturated with Lead Sulphate molecules (c in the equation), more Lead Sulphate must be precipitated.

In a similar way the strength of an acid in solution may be decreased by the addition of a substance containing a common ion. In such a case, of course, a saturated solution is not started with. Thus, in the case of the weak acid, Acetic, $HC_2H_3O_2$, under given conditions

$$\frac{a \cdot b}{c} = K.$$

The a and b represent the concentration of Hydrion, H^+, and Acetanion, $C_2H_3O_2^-$; and c the concentration of the undissociated molecules $HC_2H_3O_2$. If Potassium Acetate is added to the solution, b ($C_2H_3O_2^-$) is increased. Therefore, if the equation $\frac{a \cdot b}{c} = K$ is to hold, a must decrease or c must increase, or both of these must happen, for if the concentration of Hydrion, H^+, decreases more undissociated $HC_2H_3O_2$ must be formed. If Potassium Iodide, KI, and Potassium Iodate, KIO_3, are present in *neutral* solution, it will be found that no action takes place; but if the proper amount of Acetic Acid is added a rapid action takes place with the liberation of Iodin. If Potassium Acetate is added to the mixture, the action can be prevented or almost completely stopped, because the addition of the common ion $C_2H_3O_2^-$ (b in the equation) diminishes the Hydrion, H^+, (a in the equation) to such a degree that the action almost stops completely.

Likewise, the addition of a saturated solution of Sodium Chlorate, $NaClO_3$, to a saturated solution of Potassium Chlorate, $KClO_3$, results in the precipitation of a part of the Potassium Chlorate immediately. (Sodium Chlorate is more soluble in Water.) The increase of Chloranions, ClO_3^-, results in the combination or *association* of undissociated $KClO_3$, the ClO_3 being common to both Potassium and Sodium Chlorate. If the quantity of Sodium Chlorate added is small, a small amount of Potassium Chlorate will be precipitated; but if a large amount is added, almost all of the Potassium salt may be precipitated. From these illustrations it is readily seen that the effect of a reagent is dependent on the concentration of the reacting substances, as previously stated in the Law of Mass Action.

24. COMPLEX IONS.—It is frequently found that simple salts, especially in concentrated solutions, are capable of forming complex compounds. For example, Silver Chlorid, AgCl, is only slightly soluble in Water, but readily dissolves in dilute Ammonia Water. This is expressed by the following equation:

$$AgCl + 2NH_3 \rightleftarrows Ag(NH_3)_2Cl.$$

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A study of the properties of the Silver Ammonium Chlorid shows that it dissociates in solution as follows:

$$Ag(NH_3)_2Cl \rightleftarrows Ag(NH_3)_2^+ + Cl^-$$

To show the ionic changes involved in the above equations, the following expression is given:

$$Ag^+ + 2NH_3 \rightleftarrows (Ag(NH_3)_2)^+$$

According to the Law of Mass Action, the greater the degree of concentration of the Ammonia, the greater the tendency for the action to take place from left to right. In a 0.1 molar solution of Ammonia, the concentration of the $(Ag(NH_3)_2)^+$ ion is several times greater than the concentration of the Ag^+ ion. The complex ion, $(Ag(NH_3)_2)^+$, is decidedly different from the Ag^+ ion, just as the ClO_3^- differs from the Cl^- ion.

Similarly, when an excess of Potassium Cyanid, KCN, is added to insoluble Ferrous Cyanid, $Fe(CN)_2$, the Iron salt dissolves according to the following equation:

$$Fe(CN)_2 + 4KCN \rightarrow K_4(Fe(CN)_6)$$

This salt formed, Potassium Ferrocyanid, gives none of the ordinary reactions for Ferrous Iron, for the Iron is now a part of the complex ion, Ferrocyanidion, $Fe(CN)_6^{----}$, which has its own characteristic reactions. The stability of these complex ions varies. When very stable, the common reactions of the constituents of a complex ion are not shown.

25. Double Salts.—Complex ions may be confused with the so-called double salts. Potassium Sulphate, K_2SO_4, and Aluminium Sulphate, $Al_2(SO_4)_3$, crystallize together forming the double salt, $K_2SO_4.Al_2(SO_4)_3.24H_2O$ (also written $Al_2K_2(SO_4)_4.24H_2O$). Upon dissolving this double salt in Water, the solution shows all of the reactions for the Potassium, the Aluminium, and the Sulphate ions, and there is little, if any, evidence of the formation of a complex ion. To determine whether a substance is a double salt or a complex ion, the characteristic reactions of the simple ions are tested for. However, it is probable that there is no sharp distinction between the double salts and the salts containing complex ions, for the double salts are most likely salts which contain a complex ion that is very unstable.

26. HYDROLYSIS.—This term is used to designate the decomposing action of Water upon many salts. Since Water is a very poor conductor of electricity, the compound is dissociated to a very slight extent:

$$H_2O \rightleftarrows H^+ + OH^-$$

The cause of hydrolysis, nevertheless, is the action of the ions of Water upon the ions of a dissolved salt, and the phenomenon is represented by the following equation:

$$\underbrace{B^+ + A^-}_{\text{Salt}} + H_2O \rightleftarrows \underbrace{BOH}_{\text{Base}} + \underbrace{HA}_{\text{Acid}}$$

Heat and dilution favor hydrolysis because of the greater dissociation of Water under these conditions. That hydrolysis takes place in the cases of the following classes of salts is shown by the fact that solutions of neutral salts of Class A have an acid reaction; those of Class B, an alkaline reaction; and those of Class C sometimes acid and sometimes alkaline.

Class A. SALTS OF STRONG ACIDS AND WEAK BASES

In this case the Acid formed through hydrolysis is almost completely dissociated, while the Base formed is but slightly dissociated; therefore the reaction in aqueous solution is *acid* because of the presence of Hydrion, H^+, in appreciable amount. Examples of this class are salts of Iron, Aluminium, Chromium, etc.

Class B. SALTS OF WEAK ACIDS AND STRONG BASES

In this class the Base formed through hydrolysis is largely ionized, while the Acid is but slightly dissociated. The reaction is therefore alkaline because of the presence of Hydroxidion, OH^- in appreciable quantity. Examples of this class are the alkali salts of Boric (H_3BO_3), Carbonic (H_2CO_3), Hydrocyanic (HCN), Hypochlorous (HClO), and Sulphydric (H_2S) Acids.

Class C. SALTS OF WEAK ACIDS AND WEAK BASES

Here the Acids and the Bases formed through hydrolysis are only slightly ionized, but to different degrees. If the dissociation of the Acid is greater, the solution exhibits an acid reaction; if the dissociation of the Base is greater, an alkaline reaction. Thus, if neutral Ferric Acetate solution is *boiled*, hydrolysis takes place according to the following equation:

$$Fe(C_2H_3O_2)_3 + 2H_2O \rightleftarrows Fe(OH)_2C_2H_3O_2 + 2HC_2H_3O_2$$

The *basic* Ferric Acetate is precipitated; but if the mixture is allowed to cool there is a tendency for the action to take place in the reverse direction (right to left) and some of the basic salt goes into solution.

Class D. Salts of Strong Acids and Strong Bases

These salts give through hydrolysis, Acids and Bases which are almost entirely ionized when in dilute aqueous solution; but the Hydrion, H^+, and Hydroxidion, OH^-, are in equilibrium with non-ionized Water, and the solution is neutral in reaction and contains only as many H^+ ions and OH^- ions as correspond to the dissociation of Water, which is so small that there remains only the dissociation of the salt to be considered. Salts of this class are not subject to appreciable hydrolysis.

27. Chemical Actions of Ions.—As already stated, the large majority of actions employed in qualitative analysis are actions between ions. The student has learned that practically all chemical actions are reversible and has become familiar with some of the laws which govern this kind of chemical action. In analysis it is usually necessary to employ actions which take place almost completely in a desired direction, for unless a chemical action can be made to go almost to completion in a desired direction it is of no value as a practical test or for furnishing a method of separation. The actions applicable to qualitative analysis, then, are those which apparently go to completion. They may be divided into the following classes:

(*a*) *Those in Which a Gas Is Formed.*—When a gas is formed as the result of a chemical action, and the gas escapes, the action will go to completion. Since all gases can be boiled out of solution, all actions of this class can be made to go to completion. The fact that the action can be stopped by preventing the escape of the gas shows that the action is reversible.

(*b*) *Those in Which a Precipitate Is Formed.*—When a substance like Silver Chlorid, $AgCl$, having a very small solubility product is formed through a chemical action, the greater part of it will be precipitated and the action will go practically to completion. Thus, a saturated solution of Silver Chlorid contains about 0.00001 mole of Silver Chlorid in a Liter. Therefore by adding an excess of Chlorin ions to a solution containing Silver ions it is possible to precipitate practically all of the Silver.

(*c*) *Those in Which a Non-ionized Substance Is Formed.*—The formation of a non-ionized substance also causes an action to go to completion. Thus Calcium Phosphate dissolves in Hydrochloric Acid because more PO_4^{---} ions are formed from dissolved Calcium Phosphate than are formed from $H_2PO_4^-$ ions in the presence of an excess of H^+ ions from the Hydrochloric Acid, and the action takes place because of the formation of a non-ionized substance.

(*d*) *Those in Which Oxidation Takes Place.*—This term "Oxidation" used to be defined as the addition of Oxygen to an element. For example, when Ferr*ous* Oxid is heated in air, it is converted into Ferr*ic* Oxid, and the action is called oxidation. However, Ferr*ous* Chlorid may be converted into Ferr*ic* Chlorid, and Stann*ous* Chlorid may be converted into Stann*ic* Chlorid, and although the addition of Oxygen is not involved these also are called oxidations, therefore the present meaning of the term is decidedly more broad. The conversion of Ferr*ous* Chlorid to Ferr*ic* Chlorid by means of Chlorin may be expressed as follows:

$$2FeCl_2 + Cl_2 \rightarrow 2FeCl_3$$

or in terms of ionic theory:

$$2Fe^{++} + Cl_2 \rightarrow 2Fe^{+++} + 2Cl^-$$

That is, Diferrion is converted into Triferrion and the neutral Chlorin molecule has become converted into Chloridions.

So OXIDATION may be defined as *an increase in the valence of an element or radical in the* POSITIVE *direction.*

Oxidation involves the assumption of positive charges or the loss of negative charges. An atom of an element, according to the electronic conception of the constitution of matter, consists of positively charged corpuscles and negatively charged corpuscles. These corpuscles are also called "electrons." The mass associated with the positive electricity is much larger than that associated with the equal charge of negative electricity; and the number of electrons or corpuscles, positive and negative, which compose an atom is very likely a small multiple of the atomic weight of the element. An atom containing its positive and its negative charges is looked upon as a neutral atom. The mass associated with a unit negative charge is so small that it may easily be lost, but only when the conditions are such that it is received by some other atom. A neutral atom which loses the negatively charged electron becomes positively charged, and the atom which receives the negatively charged electron becomes negatively charged. According to this theory then, an element is oxidized when it loses a negatively charged corpuscle or electron. It should be borne in mind that the negative electricity alone is transferred and that the only way for an element to gain in the positive charge is by losing one or more negative electrons. Some of the most important OXIDIZING AGENTS are Chlorin, Bromin, Hydrogen Dioxid, Nitric Acid, Potassium Dichromate, and Potassium Permanganate.

(*e*) *Those in Which Reduction Takes Place.*—Reduction is the direct opposite to Oxidation, and, following the same line of thought in the foregoing paragraph, may be defined as *an increase in the valence of an element or radical in the negative direction.* Reduction then involves the loss of positive charges or the assumption of negative charges, and an element is reduced when it receives a negatively charged corpuscle or electron. Since any Oxidation involves a simultaneous Reduction, the examples mentioned above under Oxidation can also be used to illustrate Reduction. Another example is expressed in the following equation:

$$2Fe^{+++} + Sn^{++} \rightarrow 2Fe^{++} + Sn^{++++}$$

Triferrion or the Ferr*ic* ions are *reduced* to Diferrion or the Ferr*ous* ions; while the Stann*ous* ions are converted to Stann*ic* ions. Oxidation and Reduction actions are reversible, and like all other chemical reactions, are effected by the concentration of the reacting substances. Some of the most important REDUCING AGENTS are Nascent Hydrogen, Hydrogen Sulphid, Stannous Chlorid and Sulphurous Acid.

THE METALS, BASES, OR CATIONS

28. For simplicity, advantage is taken of the fact that certain Metals or Cations conduct themselves in a manner common to certain others and can be thrown out of solution (precipitated) by one Reagent.

The Grouping in this manual is as follows:

Group 1

LEAD, MERCURY (ous), and SILVER: Each of these Cations furnishes in solution an ION which forms an insoluble compound with the CHLORIN ION, (Cl^-) and is therefore precipitated by HYDROCHLORIC ACID or any soluble Chlorid.

Group 2

MERCURY (ic), LEAD, BISMUTH, COPPER, and CADMIUM: Each of these Cations furnishes in solution an ION which forms an insoluble compound with the SULPHUR ION (S^{--}), in the presence of Hydrogen IONS, and is therefore precipitated from ACID solutions by HYDROGEN SULPHID. Their Sulphids are *insoluble* in Ammonium Poly-sulphid.

Group 3

ARSENIC, ANTIMONY, TIN, GOLD, and PLATINUM: Each of these Cations furnishes in solution an ION which forms an insoluble compound with the SULPHUR ION in the presence of Hydrogen Ions, and is therefore precipitated, along with the Cations of Group 2, from ACID solutions by HYDROGEN SULPHID. Their Sulphids are *soluble* in Ammonium Poly-sulphid, and are separated from the Sulphids of Group 2 by this solvent.

Group 4

IRON, ALUMINIUM, and CHROMIUM: These Cations furnish in solution IONS which form insoluble compounds with the HYDROXYL ION (OH^-), and are therefore precipitated from ALKALINE solution by Ammonium HYDROXID in the presence of Ammonium Chlorid. (See ¶265, page 102.)

GROUP 5

MANGANESE, ZINC, COBALT AND NICKEL: These cations furnish in solution Ions which form insoluble compounds with the Sulphur Ion (S^{--}) in the absence of any appreciable quantities of Hydrogen Ions, and are therefore precipitated from Alkaline solution by Hydrogen Sulphid.

GROUP 6

BARIUM, STRONTIUM and CALCIUM: Each of these Cations furnishes in solution an ION which forms an insoluble compound *in warm solution* with the CARBONATE ION (CO_3^{--}), and is therefore precipitated from alkaline solution by AMMONIUM CARBONATE.

GROUP 7

SODIUM, POTASSIUM, MAGNESIUM, AMMONIUM and LITHIUM: These Cations are grouped together because all do not furnish in solution an ION which will form an insoluble compound with ONE common reagent.

TABLE I.—Group Table

<table>
<tr><td colspan="6">(If solution is <i>strongly</i> acid, evaporate to dryness on water bath, cool, and redissolve in water, using a <i>few drops</i> of HNO_3, if necessary to make a clear solution.) Add diluted HCl, in slight excess, to a clear solution of the material. Filter. (See ¶54–55.)</td></tr>
<tr><td colspan="6">(I) PRECIPITATE:—May contain AgCl, HgCl, $PbCl_2$. Wash and treat as per Table II—Group 1, page 64. (HCl Group.) (See ¶56–66.) AgCl—white. HgCl—white. $PbCl_2$—white.</td></tr>
<tr><td colspan="6">(II) FILTRATE:—May contain Groups 2, 3, 4, 5, 6, 7. If strongly acid, evaporate on water-bath to dryness; redissolve in 40 Cc. Water, using, if necessary, few drops HNO_3 to make solution clear; add 3 to 4 Cc. conc. HCl; warm nearly to boiling; then saturate with H_2S until cold. Next add 60 Cc. Water and then saturate again with H_2S. Filter. (See ¶100–102.)</td></tr>
<tr><td colspan="2">(I) PRECIPITATE:—May contain PbS, HgS, CuS, Bi_2S_3, CdS; As_2S_3, As_2S_5, Sb_2S_3, Sb_2S_5, SnS, SnS_2, Au_2S_3, PtS_2. Wash and warm with $(NH_4)_2S_x$. Filter. (See ¶ 103–105.)</td><td colspan="4">(2) FILTRATE:—May contain Groups 4, 5, 6, 7. Remove H_2S by boiling. Test original solution for PO_4^{---}, etc. by ¶ 271–272. IF PRESENT. carry out ¶ 271–276. IF ABSENT: Test small part for Iron. (¶252–253.) Next boil with Alcohol and dil. HCl until reduced to ½ bulk, then dilute with Water to original volume. Now boil with HNO_3. Add excess NH_4Cl, heat to boiling and add NH_4OH till alkaline. Filter. (¶254–255.)</td></tr>
<tr><td rowspan="3">(A) RESIDUE:—May contain PbS, HgS, CuS, Bi_2S_3. CdS. Wash and treat as per Table III—Group 2, page 77. (H_2S Group—Basic Sulphids). (See ¶106–134.)
PbS—black. HgS—black. CuS—black. Bi_2S_3—brown—black. CdS—yellow.</td><td rowspan="3">(B). FILTRATE:—May contain As, Sb, Sn, Au, Pt as Sulpho-salts (Ex: $(NH_4)_3AsS_4$) Treat as per Table IV—Group 3, page 93. (H_2S Group—Acids Sulphids.) (See ¶190–219).
As_2S_3, As_2S_5 — yellow. SnS—brown—black. SnS_2—yellow. Sb_2S_3, Sb_2S_5 — orange-red. PtS_2—brown—black. Au_2S_3—black.</td><td rowspan="3">(<i>a</i>) PRECIPITATE:—May contain $Fe(OH)_3$, $Cr(OH)_3$, $Al(OH)_3$. Wash and treat as per Table V—Group 4, page 104. (NH_4OH Group). (See ¶256–259.) In the presence of PO_4^{---}, etc., carry out ¶271–276.
$Fe(OH)_3$—red-brown, $Al(OH)_3$—white, $Cr(OH)_3$—blue-green.</td><td colspan="3">(<i>b</i>) FILTRATE:—May contain Groups 5, 6, 7. Warm; add more NH_4OH; pass in H_2S, insuring enough; heat; filter. (See ¶309–312.)</td></tr>
<tr><td rowspan="2">"a" PRECIPITATE:—May contain MnS, ZnS, NiS, CoS. Wash with weak solution of $(NH_4)_2S$ and treat as per Table VI—Group 5. page 114, (H_2S—NH_4OH Group). (See ¶312–317.)
MnS—flesh.
ZnS—black.
NiS—black.
CoS—black.</td><td colspan="2">"b" FILTRATE:—May contain Groups 6, 7. Evaporate to dryness. Heat strongly. Dissolve in enough Water to make ¾ of original bulk with aid of little HCl. Filter. Add NH_4Cl(¼ vol.), NH_4OH (till alkaline), and $(NH_4)_2CO_3$ in slight excess. Warm, let stand short time, and filter. (See ¶348–352.)</td></tr>
<tr><td>(<i>x</i>) PRECIPITATE:—May contain $BaCO_3$, $SrCO_3$, $CaCO_3$. Wash and treat as per Table VII—Group 6, page 124. $(NH_4)_2CO_3$ Group). (See ¶353–374.)
$BaCO_3$—white.
$SrCO_3$—white.
$CaCO_3$—white.</td><td>(<i>y</i>) FILTRATE:— May contain Group 7. Treat as per Table VIII——Group 7, page 135. (Alkali Group). (See ¶406–432.)
K, Na, Mg, Li.
NH_4 is tested for on original substance. (See ¶407.)</td></tr>
</table>

CHAPTER II

GROUP 1

Metals or Cations precipitated as Chlorides by Hydrochloric Acid.

LEAD (Plumbum)

Symbol, Pb^{++}. Atomic Weight, 207.2.* Valence II.

29. LEAD is a soft, malleable, bluish-gray metal. Freshly cut surfaces exhibit a metallic lustre. Fuses at 326°C. S./G., 11.38.

A solution of Lead Nitrate, $Pb(NO_3)_2$, or Lead Acetate, $Pb(C_2H_3O_2)_2$ may be used for the following tests:

TESTS

30. Hydrochloric Acid, HCl, and soluble chlorids produce in concentrated solutions heavy white precipitates of Lead Chlorid, $PbCl_2$, readily soluble in hot water. Insoluble in Ammonium Hydroxid, NH_4OH, forming a Basic Lead Chlorid. Soluble with difficulty in diluted acids.

31. Hydrogen Sulphid, H_2S, and soluble sulphids produce black precipitates of Lead Sulphid, PbS. If much free Hydrochloric Acid is present, a red precipitate of Lead Chlorosulphid is formed which is gradually converted into the black sulphid by the excess of Hydrogen Sulphid. The precipitate is insoluble in cold diluted acids, alkalis, alkali sulphids, and Potassium Cyanid. It is decomposed by hot Nitric Acid, HNO_3 forming Lead Nitrate, $Pb(NO_3)_2$, or Lead Sulphate, $PbSO_4$, or both according to the concentration of the acid.

32. Soluble iodids like Potassium Iodid, KI, produce yellow precipitates of Lead Iodid, PbI_2, soluble in excess of

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*$O = 16$.

Potassium Iodid, in fixed alkalis, Sodium Thiosulphate, $Na_2S_2O_3$, and in hot solution of Ammonium Chlorid, NH_4Cl.

33. Soluble chromates and dichromates like Potassium Chromate, K_2CrO_4, produce yellow precipitates of Lead Chromate, $PbCrO_4$, soluble in Potassium and Sodium Hydroxids, KOH and NaOH. Insoluble in Acetic Acid, $HC_2H_3O_2$.

34. Potassium Hydroxid, KOH, Sodium Hydroxid, NaOH, and Ammonium Hydroxid, NH_4OH, produce white precipitates of Lead Hydroxid, $Pb(OH)_2$, insoluble in excess of Ammonium Hydroxid, but soluble in excess of Potassium and Sodium Hydroxids, forming the plumbite ion, PbO_2^{--}. With Lead Acetate, Ammonium Hydroxid does not immediately produce a precipitate owing to the formation of soluble Basic Lead Acetate.

35. Sulphuric Acid, H_2SO_4, and soluble sulphates produce fine white precipitates of Lead Sulphate, $PbSO_4$, soluble in solution of Ammonium Acetate, $NH_4C_2H_3O_2$. Dilute solutions do not immediately give a precipitate. When admissible the addition of a few drops of Alcohol facilitates precipitation.

36. Blowpipe Test: Heated on charcoal with Sodium Carbonate, Na_2CO_3, produces a malleable globule of metallic Lead.

MERCURY (HYDRARGYRUM) IN MERCUROUS COMPOUNDS

Symbol, Hg^+. Atomic Weight, 200.6. Valence, I.

37. MERCURY is a liquid at ordinary temperatures; it is silver-white and has a bright metallic lustre. Solidifies at −39.4°C. Boiling point, 357.3°C. S/G., 13.595.

38. Mercury forms two series of compounds distinguished as Mercurous and Mercuric. In the former, Mercury is univalent, as in HgCl, Mercurous Chlorid or Calomel; in the latter series Mercury is bivalent, as in $HgCl_2$, Mercuric Chlorid or Corrosive Sublimate.

A solution of Mercurous Nitrate, $HgNO_3$, may be used in making the following tests:

TESTS

39. Hydrochloric Acid, HCl, and soluble chlorids produce white precipitates of Mercurous Chlorid, $HgCl$, insoluble in water and in dilute acids. Soluble in Nitrohydrochloric Acid, Nitric Acid, and in Chlorin Water with the formation of Mercuric Chlorid, $HgCl_2$. Sodium, Potassium, Calcium and Ammonium Hydroxids decompose the precipitate; the latter giving a black precipitate of metallic Murcury and Mercuric Aminochlorid, $HgNH_2Cl$, and the other three Hydroxids giving black Mercurous Oxid, Hg_2O.

40. Hydrogen Sulphid, H_2S, and soluble sulphids produce black precipitates of Mercurous Sulphid, Hg_2S, which breaks down into Mercuric Sulphid, HgS, and finely divided metallic Mercury. Insoluble in Potassium Cyanid, KCN; diluted acids, and Ammonium Sulphid, $(NH_4)_2S$. Readily soluble in Nitrohydrochloric Acid and Sodium Disulphid, Na_2S_2.

41. Soluble iodids like Potassium Iodid, KI, produce yellowish-green precipitates of Mercurous Iodid, HgI, partly soluble in an excess of the precipitant forming Potassium Mercuric Iodid, K_2HgI_4, and metallic Mercury.

42. Soluble chromates like Potassium Chromate, K_2CrO_4, produce bright red precipitates of Mercurous Chromate, Hg_2CrO_4 on boiling, soluble with difficulty in Nitric Acid, HNO_3.

43. Potassium Hydroxid, KOH, Sodium Hydroxid, $NaOH$, and Calcium Hydroxid, $Ca(OH)_2$, produce black precipitates of Mercurous Oxid, Hg_2O, insoluble in an excess of the precipitants. (See ¶39 for NH_4OH.)

44. A drop or two of a neutral or slightly acid solution of a Mercurous salt, when placed on a piece of clean bright Copper foil, produces a discoloration due to the deposition of metallic Mercury. Upon rubbing this with cloth the spot appears white and lustrous like silver.

45. Heated with dry Sodium Carbonate, Na_2CO_3, in a closed glass tube produces fine globules of metallic Mercury.

SILVER (ARGENTIUM)

Symbol, Ag^+. Atomic Weight, 107.88. Valence, I.

46. SILVER is a pure white, lustrous, moderately hard, very malleable metal. Fuses at 954°C. S/G., 10.575.

A solution of Silver Nitrate, $AgNO_3$, may be used for the following tests:

TESTS

47. Hydrochloric Acid, HCl, and soluble chlorids produce white, curdy precipitates of Silver Chlorid, AgCl, which become dark upon exposure to sunlight. The precipitate is soluble in Ammonium Hydroxid, NH_4OH, forming Silver Ammonium Chlorid, $Ag(NH_3)_2Cl$. Reprecipitated by adding an excess of Nitric Acid, HNO_3. Also soluble in Potassium Cyanid, KCN, forming Potassium Silver Cyanid, $KAg(CN)_2$. Soluble in concentrated Hydrochloric Acid and concentrated solution of the chlorids of the alkali metals; reprecipitated by dilution with water. Insoluble in Nitric Acid.

48. Hydrogen Sulphid, H_2S, and soluble sulphids produce black precipitates of Silver Sulphid, Ag_2S, insoluble in diluted acids, alkalis, and alkali sulphids; but soluble in Potassium Cyanid, KCN. On boiling with Nitric Acid, HNO_3, this precipitate is decomposed and dissolved, Sulphur separating.

49. Soluble iodids like Potassium Iodid, KI, produce pale, yellow precipitates of Silver Iodid, AgI, soluble in Potassium Cyanid, KCN; in very large excess of Ammonium Hydroxid, NH_4OH; and in concentrated solutions of Potassium Iodid. Insoluble in water, alcohol and diluted acids.

50. Soluble chromates like Potassium Chromate, K_2CrO_4, produce dark brownish-red, precipitates of Silver Chromate, Ag_2CrO_4, easily soluble in Nitric and Sulphuric Acids, HNO_3 and H_2SO_4, and in Ammonium Hydroxid, NH_4OH.

51. Potassium Hydroxid, KOH, and Sodium Hydroxid, NaOH, produce grayish-brown precipitates of Silver Oxid,

TABLE II—Group 1 (HCl Group)

Treat the Group Precipitate on the paper with about 20 Cc. of boiling water, and divide the *hot* filtrate into two (2) parts. (¶57.)

(1) HOT FILTRATE:—**Part 1**:—Add a few drops of H_2SO_4 and Alcohol, C_2H_5OH. A WHITE precipitate ($PbSO_4$) indicates LEAD.
Part 2:—Add a few drops of K_2CrO_4. A YELLOW precipitate ($PbCrO_4$) indicates LEAD. (¶58.)

(II) INSOLUBLE RESIDUE:—Wash with boiling water until free from Pb. Pour over it NH_4OH in two portions. Collect filtrate. (¶59.)

(1) INSOLUBLE RESIDUE:—If it is BLACK ($Hg+HgNH_2Cl$), it indicates MERCURY (ous). (¶59.)	(2) FILTRATE:—Add HNO_3 until acid. A WHITE precipitate ($AgCl$) indicates SILVER. (¶60.)

tate indicates the presence of Lead. To the second portion add a few drops of a solution of Potassium Chromate; a yellow precipitate indicates the presence of Lead.

59. The residue on the filter, insoluble in boiling water, is next washed with boiling water until free from Lead. (Test the wash water with diluted Sulphuric Acid if Lead has been found.) The wash water is rejected. The residue is then treated with Ammonium Hydroxid by pouring two portions, of about two cubic centimeters each, over it on the paper. If the residue turns black, the presence of Mercury (in the Mercurous Condition) is indicated.

60. The ammoniacal filtrate obtained by the above treatment is then treated with diluted Nitric Acid until the liquid, after shaking, has an acid reaction. (Test with litmus paper.) A white, curdy precipitate indicates the presence of Silver.

COMMENTS

61. In the foregoing separation advantage is taken of the reactions of the three metals of Group 1 with Hydrochloric Acid, and the reactions of their chlorids with Ammonium Hydroxid and water. The preliminary evaporation on a water-bath is carried out in case the solution is *strongly* acid in order to get rid of *excessive* Nitric Acid possibly present. The addition of diluted Hydrochloric Acid precipitates the Chlorids of Lead, Mercury (in the Mercurous condition) and Silver, since only these metals are capable of forming insoluble compounds with the Chlorin Ion. All three chlorids are white.

62. Care must be taken to insure the addition of a sufficient amount of Hydrochloric Acid, or some of the metals will remain in solution. However, a very large excess of the acid must be avoided since the presence of much acid would interfere with the use of Hydrogen Sulphid later, and this excess would give rise to the formation of small amounts of complex, *soluble* Silver salts.

63. The precipitate, consisting of Lead Chlorid, Mercurous Chlorid and Silver Chlorid, is then treated with boiling water in order to separate the Lead Chlorid, the only one of the three soluble in water, from the chlorids of Mercury (ous) and Silver which are insoluble.

64. The filtrate, containing only the Lead Chlorid in solution, produces insoluble white Lead Sulphate with Sulphuric Acid, and insoluble yellow Lead Chromate with Potassium Chromate.

65. The addition of Ammonium Hydroxid to the insoluble residue, consisting of the Mercurous Chlorid and Silver Chlorid, causes the decomposition of the Mercurous salt with the formation of a black precipitate of metallic Mercury and Mercuric Aminochlorid, and also dissolves the Silver Chlorid, through the formation of the soluble ion, $Ag(NH_3)_2^+$.

66. By neutralizing the Ammonium Hydroxid filtrate with Nitric Acid, Silver Chlorid is again precipitated.

CHAPTER IV

Group 2

Metals or Cations precipitated from Acid solution as Sulphids by Hydrogen Sulphid, and whose Sulphids are insoluble in Ammonium Poly-sulphid.*

MERCURY (HYDRARGYRUM) IN MERCURIC COMPOUNDS

Symbol, Hg^{++}. Atomic Weight, 200.6. Valence II.

(See MERCURY in MERCUROUS CONDITION on Page 59.)

A solution of Mercuric Chlorid, $HgCl_2$, may be used for the following tests:

TESTS

67. Hydrogen Sulphid, H_2S, and soluble sulphids in small quantities produce white precipitates of $(HgCl_2)_x(HgS)_y$, a mixture of chlorid and sulphid. Upon the further addition of the reagent the precipitate becomes yellow, orange, brownish-red. When an excess of the precipitant has been added a black precipitate of Mercuric Sulphid, HgS, is produced. The precipitate is soluble in Potassium Sulphid, K_2S, and Sodium Sulphid, Na_2S, but not in Potassium or Sodium Hydroxid. Also soluble in Aqua Regia. *Insoluble* in Ammonium Poly-sulphid, $(NH_4)_2S_x$; and Potassium Cyanid, KCN.

68. Potassium Hydroxid, KOH, and Sodium Hydroxid, NaOH, produce yellow precipitates of Mercuric Oxid, HgO. The precipitate is insoluble in an excess of the precipitant, but is soluble in diluted Hydrochloric and Nitric Acids.

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* Colorless Ammonium Sulphid—$(NH_4)_2S$. The Poly-sulphid is the yellow variety—a mixture of higher Sulphids, as $(NH_4)_2S_4$; $(NH_4)_2S_5$; $(NH_4)_2S_7$.

Small quantities of the precipitant produce a brownish-red precipitate of a basic salt.

69. Ammonium Hydroxid, NH_4OH, with a solution of Mercuric Chlorid produces a white precipitate of Mercuric Aminochlorid, $HgNH_2Cl$. The precipitate is insoluble in excess of the precipitant, but is soluble in Hydrochloric Acid, HCl; Nitric Acid, HNO_3; Acetic Acid, $HC_2H_3O_2$; Ammonium Carbonate, $(NH_4)_2CO_3$; and Sodium Thiosulphate, $Na_2S_2O_3$.

70. With metallic Copper the same reaction is produced as with Mercurous compounds. (See Page 60, ¶44.)

71. Soluble iodids like Potassium Iodid, KI, produce bright red precipitates of Mercuric Iodid, HgI_2. The precipitate is soluble in an excess of the precipitant forming, with an excess of Potassium Iodid, the complex compound, K_2HgI_4. It is also soluble in hot concentrated Nitric Acid, HNO_3; and in Sodium Thiosulphate, $Na_2S_2O_3$.

72. Stannous Chlorid, $SnCl_2$, added in small quantity to a solution of a Mercuric salt containing a small amount of Hydrochloric Acid, produces a white precipitate of Mercurous Chlorid, $HgCl$. This is converted into metallic Mercury by the addition of more of the reagent.

73. Use some dry Mercuric Chlorid, $HgCl_2$, for the following. Heated with an excess of Sodium Carbonate, Na_2CO_3, in a closed glass tube produces globules of metallic Mercury.

COPPER (CUPRUM)

Symbol, $Cu^{+};^{++}$. Atomic Weight, 63.57. Valence, I, II.

74. Copper is a reddish, lustrous, moderately hard, malleable metal. S/G., 8.94. Melting Point, 1200°C.

A solution of Copper Sulphate, $CuSO_4$, may be used for the following tests:

TESTS

75. Hydrogen Sulphid, H_2S, or a soluble sulphid, produces a brownish-black precipitate of Cupric Sulphid, CuS. The precipitate is insoluble in diluted acids and caustic alkalis. Soluble in hot Nitric Acid, HNO_3, and slightly so in Ammonium Sulphid, $(NH_4)_2S$. Also in Potassium Cyanid, KCN, forming a colorless, complex cuprous ion, $Cu(CN)_2^-$.

76. Potassium Hydroxid, KOH, and Sodium Hydroxid, NaOH, produce light blue, flocculent precipitates of Copper Hydroxid, $Cu(OH)_2$. The precipitate is insoluble in an excess of the precipitant. On boiling, the precipitate becomes brownish-black due to the formation of CuO. Soluble in Hydrochloric Acid, HCl; Nitric Acid, HNO_3; and Sulphuric Acid, H_2SO_4.

77. Ammonium Hydroxid, NH_4OH, in small amounts produces a greenish-blue precipitate of a basic cupric salt $[Cu_2(OH)SO_4]$ which is soluble in an excess of the precipitant producing a deep blue solution, due to the formation of a compound having the composition $Cu(NH_3)_4SO_4$, (ion,-$Cu(NH_3)_4^{++}$).

78. Potassium Ferrocyanid, $K_4Fe(CN)_6$, produces a reddish-brown precipitate of Copper Ferrocyanid, $Cu_2Fe(CN)_6$. The precipitate is insoluble in diluted acids, but Potassium and Sodium Hydroxid decompose it. The reagent produces only a red color in very dilute solutions.

79. Potassium Iodid, KI, produces a precipitate of Cuprous Iodid, CuI, which is whitish, but here appears dark because of the free Iodin present. The Iodin ion here acts as a reducing agent, and is itself oxidized to elementary or molecular Iodin.

80. Potassium Cyanid, KCN, produces a precipitate of Cuprous Cyanid, CuCN, which readily dissolves in an excess of the reagent because of the formation of the colorless, complex ion $Cu(CN)_2^-$. In this reaction a part of the Cyanogen ions acts as a reducing agent and passes off as free Cyanogen, $(CN)_2$. Hydrogen Sulphid, H_2S, will not precipitate the copper from this solution because the concentration of Copper as ion from the complex Cyanogen ion, $Cu(CN)_2^-$, is so small.

81. Use some dry Copper Sulphate, $CuSO_4$, for the following. Heated on Charcoal with Sodium Carbonate, Na_2CO_3, in the reducing flame produces a reddish residue of metallic Copper. Copper imparts a green color to the Bunsen flame, and from a green to blue color to the Borax Bead.

BISMUTH

Symbol, Bi^{+++}. Atomic Weight, 208. Valence, III.

82. Bismuth is a reddish-white, brittle, crystalline metal. S./G., 9.82. Melting point, 264°C.

An acid solution of Bismuth Nitrate, $Bi(NO_3)_3$, or Bismuth Chlorid, $BiCl_3$, may be used for the following tests:

TESTS

83. Hydrogen Sulphid, H_2S, and soluble sulphids produce brown precipitates of Bismuth Sulphid, Bi_2S_3. The precipitate is insoluble in diluted acids, alkalis, *alkali sulphids* and Potassium Cyanid, KCN. It dissolves in boiling Nitric Acid, HNO_3, forming Bismuth Nitrate, $Bi(NO_3)_3$, and is also soluble in hot, concentrated Hydrochloric Acid, HCl.

84. Potassium Hydroxid, KOH, and Sodium Hydroxid, NaOH, produce white, amorphous precipitates of Bismuth Hydroxid, $Bi(OH)_3$. The precipitate is insoluble in an excess of the precipitant, but soluble in Sulphuric, Nitric and Hydrochloric Acids, and in hot, concentrated, fixed hydroxides, KOH and NaOH. On heating, the precipitate turns yellow; ($Bi(OH)_3 = BiOOH + H_2O$).

85. Ammonium Hydroxid, NH_4OH, precipitates a white Basic Salt, the composition varying with the concentration and temperature.

86. Soluble carbonates like Sodium Carbonate, Na_2CO_3, produce white precipitates of Basic Bismuth Carbonate, $(BiO)_2CO_3$ or $Bi_2O(CO_3)_2$. Soluble in Hydrochloric and Nitric Acids, HCl and HNO_3. Insoluble in excess of the precipitant and in Potassium Cyanid, KCN.

87. Soluble chromates like Potassium Chromate, K_2CrO_4, give yellow precipitates of Basic Bismuth Chromate, $(BiO)_2CrO_4$. The precipitate is insoluble in Potassium Hydroxid, KOH; Sodium Hydroxid, NaOH; and diluted Acetic Acid, $HC_2H_3O_2$.

88. The addition of a large amount of water to solutions of Bismuth salts produces a white precipitate of some basic salts, as BiOCl, by hydrolysis. Much free acid interferes.

89. The addition of a solution of Stannous Chlorid, $SnCl_2$, in Sodium or Potassium Hydroxid, gives a black precipitate of metallic Bismuth.

90. Use either one of the dry Bismuth salts for the following. Heated with Sodium Carbonate, Na_2CO_3, on charcoal in the reducing flame produces a brittle globule of metallic Bismuth.

CADMIUM

Symbol, Cd^{++}. Atomic Weight, 112.4. Valence II.

91. Cadmium is a white, lustrous, ductile, malleable metal. S./G., 8.54. Melting point, 315°C.

A solution of Cadmium Nitrate, $Cd(NO_3)_2$, or Cadmium Sulphate, $CdSO_4$, may be used for the following tests:

TESTS

92. Hydrogen Sulphid, H_2S, and soluble sulphids produce bright yellow precipitates of Cadmium Sulphid, CdS. The precipitate is insoluble in diluted acids, alkalis, *Ammonium Poly-sulphid* and Potassium Cyanid, KCN. It is soluble in boiling Nitric and Hydrochloric Acids and in diluted Sulphuric Acid. The presence of much acid in a solution retards precipitation. Hastened by dilution with water.

93. Potassium Hydroxid, KOH, and Sodium Hydroxid, NaOH, produce white precipitates of Cadmium Hydroxid, $Cd(OH)_2$. The precipitate is insoluble in an excess of the precipitant, but is soluble in Hydrochloric, Nitric and Sulphuric Acids.

94. Ammonium Hydroxid, NH_4OH, produces the same result as the above, but the precipitate is readily soluble in an excess of the precipitant, forming the complex ion $Cd(NH_3)_4^{++}$.

95. Potassium Cyanid, KCN, added to a neutral or ammoniacal solution produces a white precipitate of Cadmium Cyanid, $Cd(CN)_2$. The precipitate is soluble in an excess of the precipitant forming the complex ion $Cd(CN)_4^{--}$. Hydrogen Sulphid, H_2S, precipitates the Cadmium from the solution as yellow Cadmium Sulphid, CdS.

96. Potassium Carbonate, K_2CO_2, and Sodium Carbonate, Na_2CO_3, produce white precipitates of Cadmium Carbonate, $CdCO_3$. The precipitate is insoluble in an excess of the precipitant, but is soluble in Potassium Cyanid and in Hydrochloric, Nitric and Sulphuric Acids. Ammonium salts interfere with precipitation.

97. Ammonium Carbonate, $(NH_4)_2CO_3$, produces the same precipitate as the above but the precipitate is slightly soluble in an excess of the precipitant.

98. Use either one of the dry salts for the following: Heated with Sodium Carbonate, Na_2CO_3, on charcoal in the reducing flame produces deep yellow to reddish-brown incrustations of Cadmium Oxid, CdO.

CHAPTER V

Separation of Group 2

99. After carefully studying and carrying out the tests for the metals of this Group, the student will proceed with the following separation, using a weak, acid (HCl) solution of salts of the members of this Group, or the filtrate from Group 1.

100. The filtrate obtained from Group 1 (after precipitating the metals of that Group with Hydrochloric Acid), or the solution in which Hydrochloric Acid failed to produce a precipitate, if strongly acid is evaporated to dryness on a water-bath to remove excess of acid added and Nitric Acid, if present in large amounts, and then redissolved in 40 Cc. of water using a few drops of Nitric Acid if necessary to make a clear solution. Next 3 to 4 Cc. of concentrated Hydrochloric Acid are added; it is then warmed nearly to boiling and saturated with Hydrogen Sulphid gas until cold and until it has the odor of the gas after blowing off the gas above the liquid. It is then diluted with 60 Cc. of water and saturated with Hydrogen Sulphid again.

101. This treatment will serve to precipitate Groups 2 and 3 as insoluble Sulphids. The Sulphids of Group 2 are basic in character and are insoluble in Ammonium Poly-sulphid. Those of Group 3 are acid in character and are dissolved by Ammonium Poly-sulphid.

102. The mixture is therefore filtered, and the filtrate tested with more Hydrogen Sulphid gas in order to insure that the precipitation by this reagent is complete. The precipitate is well washed with water. The filtrate, containing possibly metals of Groups 4, 5, 6 and 7, is reserved for further treatment. The wash water is rejected.

103. The washed precipitate on the paper, consisting of the Sulphids of Groups 2 and 3, is then washed from the paper into a beaker by breaking a hole in the lower part of the filter with a clean *glass rod*, and pouring a solution of Ammonium Poly-sulphid thru and thru until all the precipitate has been washed off.

104. Shake the mixture well and warm it slightly, then filter.

105. The filtrate, which contains the metals of Group 3, is reserved for treatment described in Chapter VII.

106. The residue on the paper, insoluble in Ammonium Sulphid and which consists of the Sulphids of Lead, Mercury (in Mercuric condition), Bismuth, Copper (all black) and Cadmium (yellow), is washed with water and then washed off the paper with diluted Nitric Acid, in the same way as before, into an evaporating dish. An excess of the acid must be avoided.

107. This acid mixture is boiled, adding water from time to time to replace that lost by evaporation. The mixture is heated until no further change occurs and it is then filtered. The filtrate is set aside.

108. All of the metals of this Group are dissolved with the exception of Mercury (See "Comments" on Group 2, ¶ 125.) This remains on the filter as a black precipitate. It is washed with water, removed from the paper and dissolved in a small quantity of Nitrohydrochloric Acid.

109. If the residue left after the treatment with boiling, diluted Nitric Acid is light yellow and floats on the surface, it is Sulphur and the absence of MERCURY (ic) is indicated.

110. The Nitrohydrochloric Acid mixture is heated to expell the Hydrochloric Acid and Nitrosyl Chlorid and is diluted with three or four times its volume of water.

111. After mixing thoroughly, filter, and to the filtrate add some solution of Stannous Chlorid. A white to grayish-black precipitate indicates the presence of MERCURY (ic). The filter paper and any undissolved material is rejected.

112. The filtrate obtained by boiling the Sulphides insoluble in Ammonium Poly-sulphid with diluted Nitric Acid and filtering is now examined for the remaining metals of Group 2.

113. Evaporate a small portion of this solution to free from excess of acid and increase the insolubility of the precipitate sought, add some concentrated Sulphuric Acid and allow it to stand. A white precipitate indicates the presence of LEAD.

114. If Lead is found by the foregoing treatment, the remainder of the solution is heated to expell excess of acid and then concentrated Sulphuric Acid is added. After standing, the precipitate formed is filtered out and rejected.

115. If Lead is not found, the treatment of the remainder of the solution with concentrated Sulphuric Acid is omitted.

116. The filtrate freed from Lead, or the solution with which Sulphuric Acid failed to produce a precipitate, contains the other metals of Group 2: BISMUTH, COPPER and CADMIUM. Add to it Ammonium Hydroxid until it is distinctly alkaline in reaction after shaking.

117. If a precipitate forms, filter the mixture. Reserve the filtrate and wash the precipitate well with water. Then dissolve it in a very small quantity of diluted Hydrochloric Acid. Evaporate the acid solution to a few drops, and pour it into a test-tube full of water. Allow the mixture to stand. The appearance of a milky turbidity indicates the presence of BISMUTH.

118. The filtrate obtained by adding Ammonium Hydroxid until alkaline and filtering is next examined. If it is blue, the presence of COPPER is indicated. To confirm this, evaporate a small portion nearly to dryness, add a little water and sufficient Acetic Acid to make the solution *just* acid. Then add some solution of Potassium Ferrocyanid. A reddish-brown precipitate proves the presence of COPPER.

119. If Copper is found, the balance of the filtrate is saturated with Hydrogen Sulphid gas, and then boiled with diluted Sulphuric Acid. The Copper will remain undissolved. Filter the solution and pass Hydrogen Sulphid gas thru the filtrate. A yellow precipitate indicates the presence of CADMIUM.

120. If Copper is not found, the treatment of the balance of the filtrate with diluted Sulphuric Acid is omitted, and Cadmium is tested for directly with Hydrogen Sulphid.

COMMENTS

121. In the foregoing separation advantage is taken of the reactions of the metals of this Group with Hydrogen Sulphid, and the insolubility of their Sulphids in Ammonium Poly-sulphid. It must be remembered that the Sulphids of Group 3 are precipitated with those of Group 2. These however are dissolved out by the Ammonium Poly-sulphid, and its addition serves to separate these two groups.

122. As already stated the metals of Group 1 are precipitated by Hydrochloric Acid. Mercurous Mercury and Silver are separated perfectly if the method is properly followed, but the precipitant fails to separate Lead completely, since its chlorid is *slightly* soluble in water. Therefore, it must be tested for in Group 2.

123. The addition of Hydrogen Sulphid to a solution of the acid freed residue obtained by evaporating the filtrate from Group 1, or to a solution free from the metals of that group, precipitates the Sulphids of Mercury (ic), Lead, Bismuth, Copper, Cadmium, Arsenic, Antimony, Tin, Gold and Platinum. It is important that the acidifying and saturating described in ¶100 be carried out carefully, otherwise the separation of the groups will be incomplete.

124. Upon the addition of Ammonium Poly-sulphid to the precipitate, the Sulphids of Arsenic, Antimony, Tin, Gold and Platinum (the metals of Group 3), are dissolved, leaving the Sulphids of Mercury (ic), Lead, Bismuth, Copper and Cadmium unaffected. These are removed by filtration.

125. Boiling the insoluble Sulphids of Mercury (ic), Lead, Bismuth, Copper and Cadmium with diluted Nitric Acid converts the last four sulphids to soluble nitrates. The Mercuric Sulphid remains unchanged as an insoluble residue. If only a light yellow residue that floats on the surface remains, Mercury (ic) is absent. This light yellow residue is due to the separation of Sulphur from the Ammonium Sulphid.

126. The Mercuric Sulphid is dissolved in Nitrohydrochloric Acid and forms Mercuric Chlorid, which reacts with Stannous Chlorid forming insoluble Mercurous Chlorid. An excess of the reagent converts this into metallic Mercury which appears as a grayish or black precipitate.

127. Having removed the Mercury, the filtrate, containing the remaining metals of this group, is evaporated to free from excess of Nitric Acid and increase the insolubility of the Lead Sulphate to be formed if Lead is present, and a small portion is tested for Lead by adding concentrated Sulphuric Acid. If present, a white precipitate of Lead Sulphate is formed, and the balance of the filtrate is freed from Lead by the addition of more acid, which converts all of the Lead to insoluble Lead Sulphate, while the Bismuth, Copper and Cadmium remain in solution.

128. The addition of Ammonium Hydroxid in excess to the filtrate, containing the Bismuth, Copper and Cadmium converts them to Hydroxids; those of Copper and Cadmium are soluble in an excess of the reagent, but the Bismuth Hydroxid is insoluble.

129. The precipitate, which consists of Bismuth Hydroxid, is dissolved in diluted Hydrochloric Acid and is converted to Bismuth Chlorid. After the removal of the excess of the acid, it forms the white insoluble Oxychlorid upon pouring into a test-tube of water. (This precipitate is soluble in an excess of acid.)

130. A portion of the filtrate containing the Copper and Cadmium is treated with a few drops of Potassium Ferrocyanid, after making acid with Acetic Acid. The Copper compound is converted into insoluble Copper Ferrocyanid. Only a reddish color is produced if the solution is very dilute.

TABLE III.—Group 2 (H_2S Group of Basic Sulphids)

<table>
<tr><td colspan="4">Treat the Residue, insoluble in $(NH_4)_2S_x$, with diluted HNO_3. Boil until no further change occurs and filter. (¶106–107.)</td></tr>
<tr><td colspan="4">(I) RESIDUE:—Wash and remove from paper. Dissolve in small am't. of Nitrohydrochloric Acid. Expell excess of acid by heat. Dilute with water. Filter. Add $SnCl_2$. A WHITE to GRAYISH-BLACK Precipitate (HgCl—Hg) indicates MERCURY (ic). (¶108–111.)</td></tr>
<tr><td colspan="4">(II) FILTRATE:—Evap. a small portion to free from excess of acid. Add concentrated H_2SO_4. A WHITE precipitate ($PbSO_4$) indicates LEAD. <i>If present</i>, evap. rest of filtrate and add concentrated H_2SO_4. Filter out precipitated $PbSO_4$. (If Pb is NOT found, omit treatment of remainder of filtrate with H_2SO_4.) Save filtrate. (¶112–115.)</td></tr>
<tr><td rowspan="3">(1) PRECIPITATE:—Is $PbSO_4$. Reject. (¶114.)</td><td colspan="3">(2) FILTRATE:—Add NH_4OH until alkaline. Filter. (¶116–117.)</td></tr>
<tr><td rowspan="2">(A) PRECIPITATE:—Wash. Dissolve in small am't. HCl. Evap. to a few drops and pour into cold water. Let stand. A very fine WHITE precipitate (BiOCl) indicates BISMUTH. (¶117.)</td><td colspan="2">(B) FILTRATE:—If BLUE, indicates COPPER. To confirm, add $HC_2H_3O_2$ <i>to small portion after concentration</i>, until acid, then $K_4Fe(CN)_6$. A REDDISH-BROWN precipitate ($Cu_2Fe(CN)_6$) indicates copper. (IF NOT BLUE, test for CADMIUM directly without above treatment.) <i>In the presence</i> of COPPER, saturate balance of filtrate with H_2S. Boil with diluted H_2SO_4. Filter. (¶118–119.)</td></tr>
<tr><td>(<i>a</i>) INSOLUBLE RESIDUE:—Is CuS. Reject.</td><td>(<i>b</i>) FILTRATE:—Pass thru H_2S. A YELLOW precipitate (CdS) indicates CADMIUM. (¶119–120.)</td></tr>
</table>

131. If Copper is found, the balance of the solution is treated with Hydrogen Sulphid. This converts the compounds into insoluble Sulphids.

132. Upon boiling these with diluted Sulphuric Acid, the Cadmium Sulphid is dissolved, while the Copper Sulphid remains unchanged.

133. The filtrate containing the Cadmium is treated with Hydrogen Sulphid, which precipitates yellow Cadmium Sulphid.

134. If Copper is not found by the Potassium Ferrocyanid test, the filtrate is tested directly for Cadmium with Hydrogen Sulphid.

CHAPTER VI

Group 3

Metals or Cations precipitated from Acid solution as Sulphids by Hydrogen Sulphid, and whose Sulphids are *soluble* in Ammonium Poly-sulphid.*

ARSENIC (Arsenicum)

Symbol, $As^{3+;5+}$. Atomic Weight, 74.96. Valence III, V.

135. Arsenic is a steel-gray, highly lustrous, very brittle metal. S./G., 5.727.

Arsenic forms two series of compounds: ARSENIOUS and ARSENIC compounds. They differ in a number of their important reactions.

ARSENIC in ARSENIOUS Compounds

An alkaline solution of Sodium Metarsenite, $NaAsO_2$, may be used for the following tests:

TESTS

136. Hydrogen Sulphid, H_2S, and soluble sulphids in *acid* solutions, produce bright yellow precipitates of Arsenious Sulphid, As_2S_3. Soluble in alkalis, normal alkali carbonates and *Alkali Sulphids*.

137. Silver Nitrate, $AgNO_3$, in neutral or slightly alkaline solutions, produces a bright yellow precipitate of Silver Arsenite, Ag_3AsO_3. The precipitate is soluble in Nitric Acid, HNO_3, Ammonium Hydroxid, NH_4OH and slightly so in Ammonium Nitrate, NH_4NO_3.

138. Copper Sulphate, $CuSO_4$, in neutral solutions, produces a yellowish-green flocculent precipitate of Copper

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* $(NH_4)_2S_x$.

Arsenite, $CuHAsO_3$, (Scheele's Green). The precipitate is soluble in Potassium Hydroxid, KOH; and Sodium Hydroxid NaOH; giving blue solutions in which reddish-brown precipitates of Cuprous Oxid, Cu_2O, are formed upon boiling.

139. Mixed with a small amount of Hydrochloric Acid, HCl, and heated with a perfectly clean, bright strip of Copper foil produces an iron-gray film of Copper Arsenid, Cu_5As_2, which adheres to the foil. This is a very delicate reaction and is known as the REINSCH TEST. Upon washing and drying the coated Copper foil and heating it in a dry glass tube, the Arsenic volatilizes and forms a white deposit of Arsenious Oxid, As_2O_3, on the cooler part of the tube.

140. MARSH'S TEST.—This test serves to detect very minute quantities of Arsenic. If Zinc, Water and Sulphuric Acid, H_2SO_4 or Hydrochloric Acid, HCl, are added to a solution containing Arsenic, the *very poisonous* compound Hydrogen Arsenid, AsH_3,* is formed. The test may be carried out as follows: To a flask for generating Hydrogen gas attach a tube filled with Calcium Chlorid, $CaCl_2$, to dry the gas. To this attach in a horizontal position a hard glass tube which has been drawn out at various points and which terminates in a jet. Place some metallic Zinc, *which must be free from Arsenic*, in the flask and cover with water. Then pour in a little Hydrochloric Acid, HCl, *which must also be free from Arsenic*, diluted with three parts of water. Continue adding the diluted acid until a continuous stream of Hydrogen is produced. *After making sure that all air has been expelled from the apparatus*, ignite the gas escaping at the jet. (It is advisable to cover the apparatus with a towel before lighting the jet to guard against accidents in case of an explosion.) It is now absolutely necessary to insure the absence of Arsenic in the Zinc and Hydrochloric Acid used in this test. This is done by heating the glass tube near one of the constrictions and on the side toward the generator, or by holding a porcelain dish down over the flame burning at the jet. If both Zinc and Hydrochloric Acid are NOT free from Arsenic, a black mirror will form on the tube just beyond the portion being heated, or the porcelain dish used will be coated with a brownish-black mirror. If no mirror is formed the reagents used are free from Arsenic, and the solution to be tested for Arsenic is poured into the flask through the funnel tube. The glass tube is then heated as before or a clean porcelain dish is held down over the flame from the jet. If Arsenic is present in the solution, the brownish-black deposits, described above, will form in the tube or on the dish. The deposits are *soluble* in Sodium Hypochlorite, NaClO. (Distinction from Antimony.) If the gas from the jet is passed into a solution of Silver Nitrate, $AgNO_3$, a precipitate of metallic Silver is produced. By adding to this Hydrochloric Acid, HCl, filtering, and passing Hydrogen Sulphid, H_2S, through the filtrate the Arsenic will be precipitated as yellow Arsenic Sulphid.

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* Extreme care must be observed in working with this gas.

141. Magnesia Mixture produces no precipitate with Arsenious compounds. (See Arsenic compounds.)

142. Use some dry Sodium Arsenite, $NaAsO_2$, for the following. Heated with Sodium Carbonate, Na_2CO_3 on charcoal in the reducing flame produces an odor of garlic.

ARSENIC in ARSENIC Compounds

A solution of Sodium Arsenate, Na_2HAsO_4, may be used for the following tests:

TESTS

143. Hydrogen Sulphid, H_2S, and soluble sulphids, in *acid* solutions, produce yellow precipitates of Arsenic Sulphid, As_2S_5; soluble in Ammonium Sulphid, insoluble in concentrated Hydrochloric Acid, HCl.

144. Silver Nitrate, $AgNO_3$, in neutral solutions, produces a reddish-brown precipitate of Silver Arsenate, Ag_3AsO_4. The precipitate is soluble in Nitric Acid, HNO_3 and Ammonium Hydroxid, NH_4OH, and slightly so in Ammonium Nitrate, NH_4NO_3.

145. Copper Sulphate, $CuSO_4$, added to a neutral solution, produces a bluish-green precipitate of Copper Arsenate,

$CuHAsO_4$. Soluble in an excess of Ammonium Hydroxid, and in acids.

146. With Copper foil and Hydrochloric Acid, HCl, the same result is obtained as with Arsenious compounds. (Reinsch's Test.)

147. MARSH'S TEST will give the same result as with Arsenious compounds.

148. MAGNESIA MIXTURE* produces a white crystalline precipitate of Magnesium Ammonium Arsenate, $MgHN_4AsO_4.6H_2O$. If a small portion of the precipitate is dissolved in a drop of Nitric Acid, HNO_3, and a little Silver Nitrate, $AgNO_3$, added, upon carefully neutralizing with Ammonium Hydroxid, NH_4OH, a reddish-brown precipitate of Silver Arsenate, Ag_3AsO_4, is formed.

149. Heating the dry substance on charcoal with Sodium Carbonate, Na_2CO_3, in the reducing flame will give the same results as with Arsenious compounds.

ANTIMONY (STIBIUM)

Symbol $Sb^{3+; 5+}$. Atomic Weight, 120.2. Valence, III, V.

150. Antimony is a lustrous, hard, brittle, bluish-white metal, Melting point, 425°C. S./G., 6.7.

A solution of Antimony Chlorid, $SbCl_3$, may be used for the following tests:

TESTS

151. Hydrogen Sulphid, H_2S, and soluble sulphids produce orange-red precipitates of Antimonious Sulphid, Sb_2S_3, in acid solutions. The precipitate is soluble in Potassium and Sodium Hydroxids, KOH and NaOH, *Alkali Sulphids*, and in concentrated Hydrochloric Acid, HCl. Insoluble in Ammonium Carbonate, $(NH_4)_2CO_3$. (Distinction from Arsenic.)

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* The Ammonium Chlorid in Magnesia Mixture is added to redissolve the precipitated Magnesium Hydroxid, $Mg(OH)_2$, first formed by Ammonium Hydroxid, by keeping the concentration of the hydroxyl (-OH) as ion below that necessary for the precipitation of $Mg(OH)_2$.

152. Sodium, Potassium and Ammonium Hydroxids, KOH, NaOH and NH_4OH, produce white, bulky precipitates of Antimonious Hydroxid, $Sb(OH)_3$, soluble in excess of the first two, but insoluble in excess of the last. Insoluble in solutions of Sodium, and Potassium Carbonates. Na_2CO_3 and K_2CO_3. Tartrates prevent the precipitation.

153. On pouring a solution of an Antimonious salt into a large quantity of water, a white precipitate consisting of a mixture of SbOCl and Sb_2O_3 is formed, except in the presence of large amounts of acids.

154. Mixed with a small amount of Hydrochloric Acid, HCl, and heated on a piece of bright Copper foil, yields a grayish or black film or coating on the Copper. Upon washing and drying the Copper foil and heating it in a dry glass tube, the Antimony volatilizes and forms a deposit of Antimonious Oxid, Sb_2O_3, on the cooler part of the tube. (Compare with the Reinsch Test for Arsenic.)

155. MARSH'S TEST.—Zinc and diluted Hydrochloric Acid, H_2SO_4, yield, with a solution containing Antimony, the gaseous product Hydrogen Antimonid, SbH_3. The test should be carried out in the same kind of apparatus used for making the Marsh's Test for Arsenic. On heating the tube near the contracted part, a black mirror will form as with Arsenic. By holding a porcelain dish in the ignited gas at the jet, a deposit will be obtained similar to that obtained with the Arsenic. In this case the mirror is Antimony and is *insoluble* in a solution of Sodium Hypochlorite, NaClO. (Distinction from Arsenic.) If the gas from the jet is passed into a solution of Silver Nitrate, $AgNO_3$, both Silver and Antimony are precipitated as black precipitates. The Antimony may be dissolved from this by boiling with a concentrated solution of Tartaric Acid, $H_2C_4H_4O_6$, and may be reprecipitated as an orange-red precipitate of Antimonious Sulphid, Sb_2S_3. (Compare with Marsh Test for Arsenic.)

156. Metallic Zinc reduces Antimonious solutions, the Antimony separating as a black powder. If the test is made in the presence of a piece of Platinum foil, a small piece of Zinc being placed on the foil, a black stain is formed on the

Platinum. Soluble in Nitric Acid, HNO_3. Insoluble in Hydrochloric Acid, HCl.

157. Heated on Charcoal with Sodium Carbonate, Na_2CO_3, in the reducing flame, yields brittle, white globules of metallic Antimony.

TIN (STANNUM)

Symbol, $Sn^{2+;4+}$. Atomic Weight, 118.7. Valence, II, IV.

158. Tin is a bluish-white, lustrous, soft, malleable metal. Melting point, 228°C. S./G., 7.29.

159. Tin forms two series of compounds, known respectively as STANNOUS, as SnO, Stannous Oxid; and STANNIC, as SnO_2, Stannic Oxid.

TIN in STANNOUS Compounds

A solution of Stannous Chlorid, $SnCl_2$, may be used for the following tests:

TESTS

160. Hydrogen Sulphid, H_2S, and soluble sulphids produce dark brown precipitates of Stannous Sulphid, SnS, *soluble* in Ammonium Poly-sulphid, $(NH_4)_2S_x$, forming a sulphostannate ion, SnS_3^{--}, the valence being changed to IV, but insoluble in colorless Ammonium Sulphid, $(NH_4)_2S$.

161. Sodium and Potassium Hydroxids, NaOH and KOH, produce white precipitates of Stannous Hydroxid, $Sn(OH)_2$, soluble in excess of the precipitant, forming Stannite, (SnO_2^{--}), ion.

162. Ammonium Hydroxid, NH_4OH, produces a white precipitate of Stannous Hydroxid, $Sn(OH)_2$, insoluble in excess of the precipitant.

163. A few drops of a very diluted solution of a Stannous salt added to a very diluted solution of Ammonium Molybdate, NH_4HMoO_4, form an intense blue color.

164. Mercuric Chlorid, $HgCl_2$, added in excess, produces a white precipitate of Mercurous Chlorid, HgCl, owing to the reduction of the Mercuric salt.

165. Metallic Zinc mixed with Hydrochloric Acid, HCl, produces a heavy gray precipitate of metallic Tin. If performed on a piece of Platinum foil, the metallic Tin does not adhere to the Platinum. Soluble in hot Hydrochloric Acid. (Difference from Antimony.)

166. Heated on Charcoal with Sodium Carbonate, Na_2CO_3, in the reducing flame produces white, ductile globules of metallic Tin covered with whitish SnO_2 when cooled.

TIN IN STANNIC COMPOUNDS

A solution of Stannic Chlorid, $SnCl_4$, may be used for the following tests:

TESTS

167. Hydrogen Sulphid, H_2S, and soluble sulphids produce light yellow precipitates of Stannic Sulphid, SnS_2, soluble in *Ammonium Poly-sulphid* (forming SnS_3^{--}), alkali hydroxids, and concentrated Hydrochloric Acid, HCl. Nearly insoluble in Ammonium Carbonate, $(NH_4)_2CO_3$.

168. Sodium and Potassium Hydroxids, NaOH and KOH, produce white precipitates of Stannic Hydroxid, $Sn(OH)_4$, soluble in excess, forming K_4SnO_4 or Na_4SnO_4.

169. Ammonium Hydroxid, NH_4OH, produces the same as the above, the precipitate being soluble in Potassium and Sodium Hydroxids.

170. Sodium Sulphate, Na_2SO_4, or Ammonium Nitrate, NH_4NO_3, precipitates on boiling white Stannic Hydroxid, $Sn(OH)_4$ or Metastannic Hydroxid, $(Sn(OH)_4)n$, from acid solution. (Difference from Stannous.)

171. If boiled for a long time with metallic Copper, the Stannic Chlorid, $SnCl_4$, is reduced to Stannous Chlorid, $SnCl_2$, and the solution then yields a white precipitate upon the addition of Mercuric Chlorid, $HgCl_2$.

172. Metallic Zinc reduces solutions of Stannic compounds in the same way as it does those of the Stannous compounds.

173. Heating on Charcoal in the same way as with Stannous produces ductile globules of metallic Tin.

GOLD (AURUM)

Symbol, $Au.^{+;3+}$. Atomic Weight, 197.2. Valence, I, III.

174. Gold is a yellow, lustrous, very ductile and malleable, soft metal. Melting Point, 1000°C. S./G., 19.265.

A solution of Gold Chlorid, $AuCl_3$ may be used for the following tests:

TESTS

175. Hydrogen Sulphid, H_2S, and soluble sulphids in neutral and acid solutions produce brownish-black precipitates of Gold Di-sulphid, Au_2S_2, soluble in excess of *Ammonium Poly-sulphid*, $(NH_4)_2S_x$, and in Nitrohydrochloric Acid. Also in Sodium Sulphid, Na_2S_2, and Potassium Sulphid, K_2S_2, Insoluble in Hydrochloric, HCl, and Nitric, HNO_3, Acids.

176. Sodium and Potassium Hydroxids, NaOH and KOH, produce brownish precipitates of Gold Hydroxid, $Au(OH)_3$, soluble in excess of the precipitant, forming the ion AuO_2^-.

177. Ammonium Hydroxid, NH_4OH, in concentrated solutions, produces a yellowish precipitate of Gold Iminochlorid, Au(NH)Cl, and Gold Iminoamid, $Au(NH)NH_2$ (Fulminating Gold), which when dry explodes on warming or by percussion.

178. Ferrous Sulphate, $FeSO_4$, in neutral or acid solutions, produces a brownish precipitate of finely divided Gold. The solution with the precipitate in suspension (colloidal) appears of a bluish color by transmitted light.

179. Oxalic Acid, $H_2C_2O_4$, added to a solution of a Gold salt free from Nitric Acid, HNO_3, and containing very little free acid of any kind, produces a precipitate of metallic Gold upon warming.

180. Stannous Chlorid, $SnCl_2$, in dilute weakly acid solutions, produces a purplish-red coloration or precipitate called "Purple of Cassius." It is probably colloidal Gold and Tin Oxyhydroxid. If strongly acid with Hydrochloric Acid, a dark-brown precipitate of pure Gold results.

181. Heated on Charcoal with Sodium Carbonate, Na_2CO_3, produces yellow glistening spangles of metallic Gold.

PLATINUM

Symbol, $Pt.^{2+;4+}$. Atomic Weight, 195.2. Valence, II, IV.

182. Platinum is a silver-white, lustrous, tough, very ductile and malleable metal. Melting point, 1779°C. S./G., 21.46.

A solution of Chloroplatinic Acid, H_2PtCl_6, may be used for the following tests:

TESTS

183. Hydrogen Sulphid, H_2S, and soluble sulphids, in acid solutions, produce black precipitates of Platinic Sulphid, PtS_2. The precipitate forms at once on heating the solution. Insoluble in Hydrochloric Acid, HCl, and Nitric Acid, HNO_3 but soluble in *Ammonium Poly-sulphid*, $(NH_4)_2S_x$, and Nitrohydrochloric Acid.

184. Ammonium Chlorid, NH_4Cl, produces a yellow crystalline precipitate of Ammonium Chloroplatinate, $(NH_4)_2PtCl_6$, slightly soluble in water, acids and in concentrated solutions of Potassium and Sodium Hydroxids, KOH and NaOH, on warming. Insoluble in Alcohol, C_2H_5OH. Upon ignition, a spongy residue of Platinum is produced.

185. Potassium Chlorid, KCl, produces a yellow crystalline precipitate of Potassium Chloroplatinate, K_2PtCl_6, slightly soluble in water, acids, and in concentrated solutions of Potassium and Sodium Hydroxids, KOH and NaOH, upon warming. Upon ignition, K_2PtCl_6 leaves metallic Platinum and Potassium Chlorid, KCl.

186. Ferrous Sulphate, $FeSO_4$, does not precipitate solutions of Chloroplatinic Acid, except upon very long boiling after neutralizing with Sodium Carbonate, Na_2CO_3, when a precipitate of metallic Platinum is produced.

187. Oxalic Acid, $H_2C_2O_4$, does not produce a precipitate with Platinum solutions.

188. Stannous Chlorid, $SnCl_2$, produces no precipitate but imparts a dark red to brownish-red color, if much free Hydrochloric Acid, HCl, is present. This is due to the reduction of the Chloroplatinic Acid to Chloroplatinous Acid.

189. Compounds of Platinum, heated in the reducing flame are reduced to spongy metallic Platinum.

CHAPTER VII

Separation of Group 3

190. After becoming familiar with the tests described in the last Chapter the student is ready for the separation of the metals composing this Group.

191. The student must remember that the Sulphids of this group are precipitated from acid solution, along with those of the members of the Group 2, by Hydrogen Sulphid, and that the former are soluble in Ammonium Poly-sulphid while the latter are insoluble.

192. Dilute the solution of the sulphids of the metals of this group, [which was obtained by warming the precipitate of the Groups 2 and 3 (obtained by passing Hydrogen Sulphid gas thru the filtrate from Group 1 and filtering), with Ammonium Sulphid and filtering,], *with water*. Add Hydrochloric Acid until the mixture shows an acid reaction.

193. This will precipitate the Sulphids of Arsenic, Antimony, Tin, Gold and Platinum. Filter out the precipitate and wash it thoroughly with water. The filtrate and wash water are rejected.

194. If the precipitate is white, the metals of this group are absent; the white precipitate being due to the decomposition of the Ammonium Sulphid by the Hydrochloric Acid.

195. If the precipitate is other than white, one or more of the metals of this group may be present. If bright yellow or orange-yellow, Arsenic or Antimony will very likely be found. Much Tin would cause the precipitate to be colored brown, as would Gold and Platinum.

196. Transfer the precipitate to a dish or beaker by breaking a hole in the lower end of the filter and washing it off the paper with concentrated Hydrochloric Acid. Boil the mixture and filter.

197. The Sulphids of Antimony and Tin dissolve, while those of Arsenic, Gold and Platinum remain as an insoluble residue.

198. Reserve the residue for the separation of Arsenic, Gold and Platinum as described in ¶203, and treat the Hydrochloric Acid solution as follows:

199. Warm the mixture, contained in a dish, and place in it a piece of clean Platinum foil, and on the Platinum foil a small clean piece of Zinc. If a brisk evolution of gas does not take place, add a little Hydrochloric Acid, and allow the reaction to continue for from 10 to 15 minutes.

200. Examine the Platinum foil. A deep black deposit on the foil indicates the presence of ANTIMONY.

201. To prove the presence of Tin, remove the Platinum foil and wash it with water, pouring the wash water into the dish. Remove the Zinc and rub the particles that adhere to it off into the dish. Allow the solid particles to settle and carefully pour off the supernatant liquid. Reject the liquid.

202. To the residue in the dish add a small amount of Hydrochloric Acid and heat gently. Dilute to four times its volume with water, filter if necessary, and add a few drops of a solution of Mercuric Chlorid. A white precipitate indicates the presence of TIN.

203. Going back to the residue undissolved by the boiling Hydrochloric Acid. *If this residue is bright yellow,* wash with water, and dissolve it in Ammonium Carbonate solution by pouring and repouring the carbonate solution over the residue on the paper and warming. To this add Hydrochloric Acid. A bright yellow precipitate indicates the presence of ARSENIC.

204. *If the residue is dark.* Gold and Platinum may be present. In this case carefully dry the precipitate, remove it from the paper by means of a glass spatula, and mix it with a mixture of 5 parts of Ammonium Chlorid and 1 part of Ammonium Nitrate.

205. Place this mixture in a porcelain boat, and place the boat and its contents in a glass tube which has an aspirating apparatus attached. Gradually heat the tube under the boat.

206. By this treatment the Gold and Platinum are left in the boat in the free state. The Arsenic compound is decomposed, sublimes as a chlorid, and condenses on the colder part of the tube.

207. Remove the boat from the tube and dissolve the metallic residue in Nitrohydrochloric Acid. Evaporate almost to dryness with repeated addition of Hydrochloric Acid to remove excess of Nitric Acid. Dilute with water and add an excess of Oxalic Acid. Warm the mixture for at least 30 minutes, and allow it to stand. A dark precipitate indicates the presence of Gold.

208. Filter this mixture and evaporate the filtrate almost to dryness on a water-bath. Add some diluted alcohol and filter. A dark precipitate of Ammonium Chloroplatinate indicates the presence of PLATINUM.

209. Returning to the sublimate contained in the glass tube, which may contain the ARSENIC. Dissolve the sublimate in diluted Hydrochloric Acid, and pass Hydrogen Sulphid gas thru this acid solution. The formation of a bright yellow precipitate indicates the presence of ARSENIC.

COMMENTS

210. The Sulphids of Group 3, as already stated, are separated from those of Group 2, with which they are precipitated by Hydrogen Sulphid, by *yellow* Ammonium Sulphid, in which they are soluble.

211. The addition of Hydrochloric Acid to the filtrate serves to neutralize the solvent effect of the fluid, and the Sulphids of Arsenic, Antimony, Tin, Gold and Platinum are reprecipitated in the now acid fluid. The precipitate is now washed *thoroughly* in order to remove Hydrochloric Acid, Hydrogen Sulphid and Chlorids, as their presence may interfere with subsequent tests.

212. Since the Sulphid of Arsenic is yellow; that of Antimony orange-red; Tin, brown; Gold, brownish-black; and Platinum, black; the presence of a white precipitate would indicate the absence of this group, the white precipitate being Sulphur, as explained in the Separation.

213. Boiling the precipitate with concentrated Hydrochloric Acid serves to dissolve the Sulphids of Antimony and Tin, but not those of Arsenic, Gold and Platinum, since these are insoluble in the acid.

214. The filtrate, containing the Antimony and Tin as Chlorids, is treated with Zinc, a little more Hydrochloric Acid, and a piece of Platinum foil, taking advantage of the reducing reactions described in ¶156 for Antimony, Page 83, and ¶165 for Tin, Page, 85. The Antimony is deposited as a black stain on the Platinum, while the Tin is precipitated as a heavy gray precipitate.

215. The precipitated Tin is heated with Hydrochloric Acid which converts it to soluble Stannous Chlorid. This in turn reacts with a solution of Mercuric Chlorid which is reduced to insoluble Mercurous Chlorid.

216. If the residue insoluble in the boiling Hydrochloric Acid is bright yellow, it indicates Arsenic, since its Sulphid is of a bright yellow color, while those of Gold and Platinum are blackish. If yellow, the presence of Arsenic is confirmed by dissolving the yellow Sulphid in Ammonium Carbonate and reprecipitating it by Hydrochloric Acid.

217. A dark precipitate at this point would indicate the possible presence of Gold and Platinum. In order to separate the Arsenic, possibly present, from the Gold and Platinum, the precipitate is dried, mixed with Ammonium Nitrate and Chlorid, and subjected to the process described in the Separation, since the Arsenic sublimes as a Chlorid, and the Gold and Platinum are left in the boat in the free condition.

218. The metallic Gold and Platinum are dissolved in Nitrohydrochloric Acid, and the excess of Nitric Acid removed by evaporation and the addition of Hydrochloric

TABLE IV.—Group 3 (H_2S Group of Acid Sulphids)

<table>
<tr><td colspan="5">Dilute the Filtrate (obtained by treating the precipitate resulting from the H_2S treatment of the filtrate from Group 1 with $(NH_4)_2S_x$ and filtering) with water and add HCl until acid. Filter. Wash the precipitate. <i>Reject the filtrate.</i> (¶192–193.)</td></tr>
<tr><td colspan="5">PRECIPITATE:—If WHITE, the members of this Group are absent, since their Sulphids are colored.
If other than WHITE, wash off the paper with concentrated HCl and boil. Filter. (¶194–198.)</td></tr>
<tr><td rowspan="3">I
F

D
A
R
K</td><td colspan="2">(1) INSOLUBLE RESIDUE:—Wash. (<i>A</i>)—If bright YELLOW, dissolve in $(NH_4)_2CO_3$. Add HCl. A bright YELLOW precipitate (As_2S_5) indicates ARSENIC. (¶203.)
(<i>B</i>) If DARK, dry and mix with 5 of NH_4Cl and 1 of NH_4NO_3. Place in porcelain boat and heat in glass tube. (¶204–206.)
(A) Dissolve contents of boat in Nitrohydrochloric Acid. Evap. with HCl to remove excess of acid. Dilute with water, and add excess of Oxalic Acid, $H_2C_2O_4$. Warm 30 minutes. Let stand. Filter. (¶207.)</td><td colspan="2">(2) FILTRATE:—Warm in a dish with Pt foil and piece of Zn. Keep up reaction for 10–15 minutes. (¶199.) A deep BLACK deposite (Sb) on the Pt indicates ANTIMONY. (¶200.)
——
Remove Pt foil; wash it with water, collecting washings in same dish. Rub off particles adhering to Zn into dish. Reject Zn. Let solid matter settle. Decant liquid. (¶201.)</td></tr>
<tr><td>(<i>a</i>) PRECIPITATE: Is metallic Au, and indicates GOLD. (¶207.)</td><td>(<i>b</i>) FILTRATE:—Evap. almost to dryness. Add diluted C_2H_5OH. A DARK precipitate ($(NH_4)_2PtCl_6$) indicates PLATINUM. (¶208.)</td><td rowspan="2">(<i>a</i>) LIQUID:—Reject.</td><td rowspan="2">(<i>b</i>) RESIDUE:—Add small am't. HCl and warm. Dilute with water. Filter if necessary. Add a few drops of $HgCl_2$. A WHITE precipitate (HgCl) indicates TIN. (¶202.)</td></tr>
<tr><td colspan="2">(B) Dissolve the sublimate in the glass tube in dil. HCl. Pass thru H_2S. A BRIGHT YELLOW precipitate (As_2S_5) indicates ARSENIC. (¶209.)</td></tr>
</table>

Acid. The metals go into solution as Chlorids. Upon warming with Oxalic Acid the Gold separates out, as described in Chapter VI (at this point the mixture should be warmed a long time to insure the complete precipitation of the Gold); while the Platinum remains uneffected and is tested for in the filtrate by evaporating to dryness and treating the residue with diluted alcohol, thereby removing the excess of Oxalic Acid and Ammonium Chlorid. The Platinum remains behind as Ammonium Chloroplatinate.

219. The sublimate, containing the Arsenic as a Chlorid, is dissolved in Hydrochloric Acid and reprecipitated as yellow Sulphid by Hydrogen Sulphid.

CHAPTER VIII

Group 4

Metals or Cations precipitated by Ammonium Hydroxid in the presence of Ammonium Chlorid as Hydroxids.

IRON (FERRUM)

Symbol, Fe. $^{2+}$; $^{3+}$. Atomic Weight, 55.84. Valence, II, III.

220. Pure IRON is a silver-white, hard, malleable, ductile, tenacious metal. Melting Point, 1510°C. S./G., 7.84.

221. Iron forms two series of compounds, named respectively FERROUS and FERRIC compounds. Ferrous Oxid, FeO, is a type of the former; and Ferric Oxid, Fe_2O_3, a type of the latter.

IRON IN FERROUS COMPOUNDS

A solution of Ferrous Sulphate, $FeSO_4$, may be used for the following tests:

TESTS

222. Ammonium Sulphid, $(NH_4)_2S$, or Hydrogen Sulphid, H_2S, in neutral or alkaline solutions, produce black precipitates of Ferrous Sulphid, FeS, soluble in Hydrochloric Acid, HCl, and Nitric Acid, HNO_3. Acid solutions of Ferrous salts are not precipitated by H_2S. Ammonium Chlorid, NH_4Cl, promotes precipitation.

223. Potassium Hydroxid, KOH, or Sodium Hydroxid, NaOH, produce a precipitate of Ferrous Hydroxid, $Fe(OH)_2$, which is white at first, but which, upon exposure to air, becomes green and finally reddish-brown, due to oxidation to Ferric Hydroxid, $Fe(OH)_3$. Presence of Ammonium salts interferes with complete precipitation. Soluble in acids.

224. Ammonium Hydroxid, NH_4OH, gives the same precipitate as the preceding.

225. Potassium Thiocyanate, KCNS, does not produce a blood-red coloration in solution of Ferrous salts free from Ferric salts.

226. Potassium Ferrocyanid, $K_4Fe(CN)_6$, produces a white precipitate of Potassium Ferrous Ferrocyanid, $K_2Fe(Fe(CN)_6)$, insoluble in acids. Excess of reagent converts this into Ferrous Ferrocyanid, $Fe_2(Fe(CN)_6)$. This, thru oxidation, becomes rapidly blue in color, Ferric Ferrocyanid, $Fe_4(Fe(CN)_6)_3$ (Prussian Blue), being formed.

227. Potassium Ferricyanid, $K_3Fe(CN)_6$, produces a dark blue precipitate of Ferrous Ferricyanid, $Fe_3(Fe(CN)_6)_2$, (Turnbull's Blue), mixed with Potassium Ferric Ferrocyanid. The precipitate is insoluble in acids.

228. Dry Ferrous Compounds, heated in a Borax Bead in the oxidizing flame, produce, while hot, a yellow to red bead, which on cooling becomes lighter in color or colorless. Fused in the reducing flame yield a bottle-green bead.

IRON IN FERRIC COMPOUNDS

A solution of Ferric Chlorid, $FeCl_3$, may be used for the following tests:

TESTS

229. Ammonium Sulphid, $(NH_4)_2S$, or Hydrogen Sulphid, H_2S, form Fe_2S_3 only when added to Ferric Hydroxid, $Fe(OH)_3$, in the presence of an alkali. With acid solutions part of the Sulphid is reduced to FeS, and Sulphur, S, is precipitated ($2FeCl_3 + H_2S \rightarrow 2FeCl_2 + 2HCl + S$). The precipitate is black, insoluble in alkali hydroxids; soluble in acids.

230. Potassium and Sodium Hydroxids, KOH and NaOH, produce bulky, reddish-brown precipitates of Ferric Hydroxid, $Fe(OH)_3$, insoluble in excess of the precipitant and in Ammonium salts, but soluble in Hydrochloric, Nitric and Sulphuric Acids, HCl, HNO_3, and H_2SO_4.

231. Ammonium Hydroxid, NH_4OH, produces the same result as the preceding.

232. Potassium Thiocyanate, KCNS, produces an intense blood-red coloration, due to the formation of Ferric Thiocyanate, $Fe(CNS)_3$.

233. Potassium Ferrocyanid, $K_4Fe(CN)_6$, produces a dark blue precipitate of Ferric Ferrocyanid, $Fe_4(Fe(CN)_6)_3$ (Prussian Blue), insoluble in Hydrochloric Acid, HCl, but decomposed by alkali hydroxids.

234. Potassium Ferricyanid, $K_3Fe(CN)_6$, does not produce a precipitate in solutions of Ferric salts, but deepens the color to reddish-brown, Ferric Ferricyanid being formed.

235. With the Borax Bead, Ferric Compounds produce the same results as the Ferrous.

CHROMIUM

Symbol, Cr. $^{2+;3+}$. Atomic Weight, 52. Valence, II, III.

236. CHROMIUM is a light gray, crystalline powder. Melting Point, above 2000°C. S./G., 6.81.

A solution of Chromic Chlorid, $CrCl_3$, may be used for the following tests:

TESTS

237. Ammonium Sulphid, $(NH_4)_2S$, in neutral or slightly acid solution, produces a greenish or bluish precipitate of Chromium Hydroxid, $Cr(OH)_3$ (Hydrolysis). Soluble in Hydrochloric Acid, HCl.

238. Potassium and Sodium Hydroxids, KOH and NaOH, produce greenish precipitates of Chromium Hydroxid, $Cr(OH)_3$, soluble in excess of the reagents. By boiling, or by the addition of Ammonium Chlorid, NH_4Cl, the Hydroxid is reprecipitated.

239. Ammonium Hydroxid, NH_4OH, produces the same precipitate as the preceding. The precipitate is slightly soluble in excess, but is completely precipitated upon boiling.

240. Sodium, Potassium and Ammonium Carbonates, Na_2CO_3, K_2CO_3, $(NH_4)_2CO_3$, produce green precipitates of Chromium Hydroxid, $Cr(OH)_3$ (Hydrolysis), slightly soluble in large excess of the reagents, and in Hydrochloric Acid.

241. Bromin Water, added to a solution of a Chromium salt, which contains an excess of Sodium or Potassium Hydroxid, NaOH or KOH, and warmed, produces a change in color from green to yellow, due to the formation of a Chromate of the alkali used.

242. Fused on a Platinum foil with Sodium Carbonate, Na_2CO_3, and Potassium Nitrate, KNO_3, in the oxidizing flame, produces a yellow mass due to the formation of Sodium Chromate, Na_2CrO_4, and Potassium Chromate, K_2CrO_4. By dissolving the mass in water, and adding Acetic Acid, $HC_2H_3O_2$, and Lead Acetate, $Pb(C_2H_3O_2)_2$, a yellow precipitate of Lead Chromate, $PbCrO_4$, is produced.

243. Dry Chromium compounds, heated in a Borax Bead, produce a yellowish-green bead, which becomes emerald green on cooling.

ALUMINIUM

Symbol, Al^{+++}. Atomic Weight, 27.1. Valence, III.

244. ALUMINIUM is a bluish-white, lustrous, malleable, ductile metal. Melting Point, 700°C. S./G., 2.71.

A solution of Potassium Aluminium Sulphate, $KAl(SO_4)_2$, or Ammonium Aluminium Sulphate, $NH_4Al(SO_4)_2$, may be used for the following tests:

TESTS

245. Ammonium Sulphid, $(NH_4)_2S$, produces a white, gelatinous precipitate of Aluminium Hydroxid, $Al(OH)_3$, slightly soluble in excess of the reagent. (Hydrolysis.) Soluble in Hydrochloric, Nitric and Sulphuric Acids.

246. Potassium and Sodium Hydroxids, KOH and NaOH, produce white, gelatinous precipitates of Aluminium Hydroxid, $Al(OH)_3$, soluble in excess of the reagents with formation of Potassium Aluminate, $KAlO_2$ or Sodium Aluminate, $NaAlO_2$. Reprecipitated by Ammonium Chlorid, NH_4Cl, and heating.

247. Ammonium Hydroxid, NH_4OH, produces the same precipitate as the preceding. The precipitate is slightly soluble in excess of the reagent. The solubility is decreased by presence of Ammonium salts and by boiling.

248. Di-sodium Hydrogen Phosphate, Na_2HPO_4, produces a white, gelatinous precipitate of Aluminium Phosphate, $AlPO_4$, insoluble in Acetic Acid, $HC_2H_3O_2$, and Ammonium Hydroxid. Soluble in Hydrochloric and Nitric Acids, HCl and HNO_3. Soluble also in Potassium Hydroxid, and Sodium Hydroxid, KOH and $NaOH$, with formation of Aluminates $KAlO_2$ or $NaAlO_2$. Ammonium Chlorid, NH_4Cl, reprecipitates the Aluminium Phosphate from its solution in Potassium or Sodium Hydroxid.

249. Sodium Acetate, $NaC_2H_3O_2$, added in excess and boiled, produces a precipitate of Basic Aluminium Acetate, $Al(OH)_2C_2H_3O_2$. Neutral Aluminium Acetate is at first formed but this decomposes on boiling to yield the basic compound. The precipitate dissolves on cooling.

250. Barium Carbonate, $BaCO_3$, mixed with a little water, produces a white gelatinous precipitate of Aluminium Hydroxid, $Al(OH)_3$, with a solution of an Aluminium salt. (Hydrolysis.) It is insoluble in excess of the reagent.

251. Dry Aluminium salts, heated on charcoal with Sodium Carbonate, Na_2CO_3, then moistened with Cobalt Nitrate, $Co(NO_3)_2$, and ignited, produce a blue mass, due to the formation of a complex compound called Thenard's Blue.

CHAPTER IX

Separation of Group 4

252. The filtrate from Groups 2 and 3, or a solution free from the members of the first three groups should be treated as follows. If Hydrogen Sulphid has been added to precipitate Groups 2 and 3, this must be completely removed by prolonged boiling before Group 4 can be precipitated or Group 5 will be precipitated with Group 4. To determine when all the Hydrogen Sulphid has been removed, hold a piece of filter paper moistened with Lead Acetate solution in the steam. If this is blackened, Hydrogen Sulphid is still being given off.

253. Having removed the Hydrogen Sulphid, test a small portion of the original solution for Phosphates, Oxalates and Tartrates according to ¶271–272. If present, the method described in ¶273–276 must be carried out. If absent, proceed as follows. Test one small portion of the solution for Ferrous Iron (ion Fe^{++}) by adding Hydrochloric Acid and some fresh solution of Potassium Ferricyanid. If Ferrous Iron is present a dark blue precipitate will form (Ferrous Ferricyanid, $Fe_3(Fe(CN)_6)_2$). Test another small part for Ferric Iron (ion Fe^{+++}) by adding Hydrochloric Acid and a solution of Potassium Thiocyanate. If Ferric Iron is present a *deep, blood-red* color will develop (undissociated Ferric Thiocyanate $Fe(CNS)_3$). If iron is found, test the original solution to determine the state of oxidation.

254. Next boil the solution with Alcohol and diluted Hydrochloric Acid to reduce the Chromate or Dichromate ions (the condition in which Chromium may be at this point if no Hydrogen Sulphid has been used) until reduced to about one-half the original volume to drive off all Alcohol, and then dilute to original volume with Water. However, if Hydrogen Sulphid has been used to precipitate Groups 2 and 3, this treatment with Alcohol is unnecessary. The Iron, if present in the Ferrous condition, must next be oxidized by boiling the solution with Nitric Acid.

255. Then add an excess of Ammonium Chlorid,* heat to boiling and add Ammonium Hydroxid until the mixture has a strong alkaline reaction. Filter and reserve the filtrate if the members of Groups 5, 6, and 7 are to be tested for. Treat the precipitate, which consists of the Hydroxids of Iron, Aluminium and Chromium, as follows:

256. Wash the precipitate with hot water *thoroughly*, place in a dish, add a small amount of water and about 2 Gm. of Sodium Dioxid, and boil for a minute. Filter and divide the filtrate into two parts. Reserve the undissolved residue, if there should be any.

257. Test one part for Aluminium by making acid with Hydrochloric Acid, then alkaline with Ammonium Hydroxid, and heating to boiling. If Aluminium is present, a white, flocculent precipitate is formed. The precipitate may be more readily seen if the mixture is allowed to stand a short time.

258. Test the other part for Chromium by making acid with Acetic Acid and adding Lead Acetate solution. In the presence of CHROMIUM, a *yellow* precipitate will form. (If the filtrate to be tested for Chromium is colorless, Chromium is absent, since all Chromates and Dichromates are colored.)

259. The residue left undissolved by Sodium Dioxid, consisting of Ferric Hydroxid (reddish-brown), should be tested for Manganese, which is likely to be partially precipitated here, especially if too much Nitric Acid was used to oxidize the Iron. Dry the residue, fuse it with Sodium Carbonate and Potassium Nitrate in the oxidizing flame. In the presence of Manganese a blue-green mass (Na_2MnO_4 and K_2MnO_4) will form. The student must become familiar with the color imparted by Manganese, for he may be confused because of the Iron simulating the color.

COMMENTS

260. The filtrate from Groups 2 and 3, contains the members of Groups 4, 5, 6 and 7. In order to precipitate

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*See ¶265.

Group 4 by itself, the Hydrogen Sulphid used to precipitate Groups 2 and 3 must be removed for the reason stated in the separation.

261. Since a solution of the members of Group 4 may contain Iron as Ferrous or Ferric ions or both, and the Chromium as Chromic, Chromate or Dichromate ions, it is necessary, in order to precipitate these metals by Ammonium Hydroxid to carry out the steps described in ¶253–255.

262. Special tests for the condition of Iron in the original solution must be made on portions of the ***original*** solution, since the Iron has possibly undergone changes during the steps already taken.

263. Since the Chromate and Dichromate ions do not form compounds with Hydroxyl, it is necessary, in the presence of these ions, to reduce them to Chromic ions. This may be done by passing Hydrogen Sulphid thru an acid solution, but is accomplished more easily by boiling with Alcohol and diluted Hydrochloric Acid until reduced to one-half the original bulk.

264. Since Ferrous Hydroxid is only incompletely precipitated by Ammonium Hydroxid, boiling with Nitric Acid is carried out next to oxidize to the Ferric condition.

265. Having reduced the Chromate ion and oxidized the Iron, an excess of Ammonium Chlorid is added to keep the concentration of Hydroxyl ions below that necessary for the precipitation of Magnesium and Manganese Hydroxids; and enough Ammonium Hydroxid to give a strong alkaline reaction is added, thereby furnishing Ammonia for the formation of complex ammonia ions of Zinc, Nickel and Cobalt, so redissolving their Hydroxids.

266. Filtering separates the members of Groups 5, 6 and 7 (which are in the filtrate) from the precipitated Hydroxids of Iron, Aluminium and Chromium.

267. After washing the precipitate, it is boiled with Sodium Dioxid to oxidize Chromic ions to Chromate. The Aluminium Hydroxid is dissolved by the Sodium Hydroxid formed by the action of Sodium Dioxid on the water, and the Ferric Hydroxid is unaffected.

268. One part of the filtered fluid is tested *immediately*, to avoid dissolving Silica from the vessel, for Aluminium. The Hydrochloric Acid is added to neutralize the Sodium Hydroxid, and the Ammonium Hydroxid is then added and the mixture boiled to precipitate the Aluminium.

269. Chromium is then tested for by making the second part acid and adding Lead Acetate. The *yellow* precipitate formed in the presence of Chromium is Lead Chromate. If the precipitate formed at this point is white, it is Lead Sulphate and indicates that the original precipitate of the Hydroxids of the members of this group was not thoroughly washed. A white precipitate does not indicate Chromium.

270. Manganese, a member of Group 5, is tested for in the insoluble residue for the reason given in the separation.

METHOD OF SEPARATING GROUP 4 IN THE PRESENCE OF THE PHOSPHATE (PO_4^{---}), OXALATE ($C_2O_4^{--}$), AND TARTRATE ($C_4H_4O_6^{--}$) IONS.

271. The presence of these ions should be first established by treating a portion of the *original solution* with Sodium Carbonate until strongly alkaline, boiling for 15 minutes, and then filtering. This serves to precipitate the metals (with the exception of the members of Group 7) which would interfere with the test for these ions. Reject the precipitate.

272. Test one portion of the filtrate by making acid with Nitric Acid and applying the test described in ¶454 for the Phosphate ion. Test another portion for the Oxalate ion by making acid with Acetic Acid and applying the test described in ¶497. Test a third portion for the Tartrate ion by ¶505.

273. Having established the presence of these ions in the *original solution*, evaporate the *filtrate from Groups* 2 *and* 3 to dryness; add a few drops of Nitric Acid and ignite gently.

TABLE V.—Group 4 (NH_4OH Group)

* Wash Group precipitate *thoroughly* with hot water, place in dish, add a little water and 2 Gm. Na_2O_2, and boil a minute. Filter. (¶256.)		
(I) INSOLUBLE RESIDUE:—Reddish-brown, $Fe(OH)_3$, indicates IRON. (The original sol. is tested for condition of Iron, ¶253.) Test for Manganese by fusing with Na_2CO_3 and KNO_3. A BLUE-GREEN color (Na_2MnO_4 and K_2MnO_4) indicates MANGANESE. (¶259.)	(II) FILTRATE:—Divide into 2 parts. (¶256.)	
	(I) PART 1: Test immediately. Add HCl till acid, then NH_4OH till alkaline, boil. A WHITE, flocculent precipitate ($Al(OH)_3$) indicates ALUMINIUM. (¶257.)	(2) PART 2: Add Acetic Acid till acid, then Lead Acetate, $Pb(C_2H_3O_2)_2$. A YELLOW precipitate ($PbCrO_4$) indicates CHROMIUM. (¶258.)

*NOTE.—In the presence of PO_4^{---}, $C_2O_4^{--}$, and $C_2H_4O_6^{--}$, ¶271-276 must be carried out.

Ignition carbonizes the Tartrate salts, the black residue (C) from these is consumed. Then warm the residue with diluted Hydrochloric Acid and filter. Reject any undissolved matter.

274. Test a small portion of the filtrate for Iron by adding Potassium Thiocyanate. The formation of a *deep* blood-red color indicates IRON. If Iron is found, determine its state of oxidation in the original solution by ¶226 and ¶232.

275. Add to the remainder of the filtrate an excess of Sodium Acetate solution, make strongly acid with Acetic Acid; and add drop by drop solution of Ferric Chlorid till the solution becomes *decidedly* red, because of the formation of Ferric Acetate. Next boil for 5 minutes. This precipitates the Iron and a part of the Aluminium and Chromium as phosphates (ortho). Filter while hot. *Reserve the filtrate.*

276. Wash the precipitate with hot water and test the precipitate for Aluminium and Chromium by ¶256-258. The filtrate from the precipitated phosphates is liable to contain Aluminium, Chromium, and the members of Groups 5, 6 and 7, and should be examined for these in the regular order, beginning with ¶252.

CHAPTER X

Group 5

Metals or Cations precipitated as Sulphids by Hydrogen Sulphid in *Alkaline* solution.

MANGANESE

Symbol, $Mn^{2+;\ 3+}$. Atomic Weight, 54.93. Valence, II, III.

277. MANGANESE is a grayish-white, very hard, brittle metal. Melting Point, 1247°C. S./G., 7.8.

A solution of Manganous Sulphate, $MnSO_4$, or Manganous Chlorid, $MnCl_2$, may be used for the following tests:

TESTS

278. Ammonium Sulphid, $(NH_4)_2S$, or Hydrogen Sulphid, H_2S, in alkaline solutions, produce flesh colored precipitates of Manganous Sulphid, MnS, which become brown thru oxidation in air. Soluble in Hydrochloric Acid, HCl, Nitric Acid, HNO_3, and Acetic Acid, $HC_2H_3O_2$. Insoluble in Ammonium Sulphid and alkali hydroxids.

279. Potassium and Sodium Hydroxids, KOH and NaOH, produce whitish precipitates of Manganous Hydroxid, $Mn(OH)_2$, insoluble in excess of the reagent. ($Mn(OH)_3$ is precipitiated from solutions containing the manganic ion.) Soluble in Hydrochloric, Nitric and Sulphuric Acids, HCl, HNO_3, and H_2SO_4; also in Ammonium salts. Upon exposure to air the precipitate turns brown, due to the formation of Manganous Manganites.

280. Ammonium Hydroxid, NH_4OH, produces the same result as the preceding, except in the presence of Ammonium salts, because the large concentration of Ammonium ion represses the concentration of the Hydroxyl ion.

281. Sodium, Potassium and Ammonium Carbonates, Na_2CO_3, K_2CO_3, $(NH_4)_2CO_3$, produce white precipitates of Manganous Carbonate, $MnCO_3$. The precipitate is insoluble in excess of the reagent.

282. Bromin Water, added to a solution of a Manganese salt which contains an excess of Sodium or Potassium Hydroxid, NaOH or KOH, produces a brownish-black precipitate of Hydrated Manganese Dioxid, $MnO_2.H_2O$.

283. Dry Manganese compounds, fused on a Platinum foil with Sodium Carbonate, Na_2CO_3, and Potassium Nitrate, KNO_3, in the oxidizing flame, produce a bluish-green mass, due to the formation of Sodium Manganate, Na_2MnO_4, and Potassium Manganate, K_2MnO_4. The same result is obtained by using Sodium Peroxid, Na_2O_2.

284. Manganese compounds, fused in a Borax Bead in the oxidizing flame, produce an amethyst-colored bead; in the reducing flame a colorless bead.

ZINC (ZINCUM)

Symbol, Zn^{++}. Atomic Weight, 65.37. Valence, II.

285. ZINC is a bluish-white, rather soft metal. Melting Point, 417°C. S./G., 6.9.

A solution of Zinc Sulphate, $ZnSO_4$, or Zinc Nitrate, $Zn(NO_3)_2$, may be used for the following tests:

TESTS

286. Ammonium or Hydrogen Sulphids produce a white precipitate of Zinc Sulphid, ZnS. Precipitation is aided by Ammonium Chlorid, NH_4Cl. The precipitate is soluble in Hydrochloric, Nitric and Sulphuric Acids, HCl, HNO_3, and H_2SO_4. Insoluble in diluted Acetic Acid, $HC_2H_3O_2$; Ammonium Sulphid, $(NH_4)_2S$; and alkali hydroxids.

287. Potassium and Sodium Hydroxids, KOH and NaOH, produce white, gelatinous precipitates of Zinc Hydroxid, $Zn(OH)_2$, soluble in excess of the reagent with formation of Sodium Zincate, Na_2ZnO_2, or Potassium Zincate,

K_2ZnO_2. Reprecipitated upon boiling, unless the precipitants have been added in very large excess. Soluble in Hydrochloric, Nitric and Sulphuric Acids, HCl, HNO_3, and H_2SO_4.

288. Ammonium Hydroxid, NH_4OH, produces a white precipitate of Zinc Hydroxid, $Zn(OH)_2$, soluble in excess of the precipitant forming a soluble compound having the complex ion Zinc-Ammonia, $Zn(NH_3)_6^{++}$.

289. Potassium Ferrocyanid, $K_4Fe(CN)_6$, produces a white slimy precipitate of Zinc Ferrocyanid, $Zn_2Fe(CN)_6$, slightly soluble in excess of the precipitant; insoluble in acids and Ammonium Hydroxid, NH_4OH.

290. Potassium Ferricyanid, $K_3Fe(CN)_6$, produces a brownish-yellow precipitate of Zinc Ferricyanid, $Zn_3(Fe(CN)_6)_2$, soluble in acids.

291. Di-sodium Hydrogen Phosphate, Na_2HPO_4, produces a white precipitate of Zinc Phosphate, $Zn_3(PO_4)_2$, which is gelatinous when first formed, but becomes crystalline upon standing. Soluble in acids and Ammonium Hydroxid, NH_4OH.

292. Dry Zinc salts, heated with Sodium Carbonate, Na_2CO_3, on charcoal in the reducing flame, produce a coating of Zinc Oxid, ZnO, which is yellow while hot and white when cold. On moistening with a solution of Cobalt Nitrate, $Co(NO_3)_2$, and igniting, a bright yellow-green coat is produced.

COBALT

Symbol, $Co^{2+;3+}$. Atomic Weight, 58.97. Valence, II, III.

293. Cobalt is a steel-gray, hard, malleable metal. Melting Point, 1600°C. S./G., 8.5.

A solution of Cobalt Nitrate, $Co(NO_3)_2$ or Cobalt Sulphate, $CoSO_4$, may be used for the following tests:

TESTS

294. Ammonium Sulphid, $(NH_4)_2S$, or Hydrogen Sulphid, H_2S, in neutral or alkaline solution produce black precipitates of Cobalt Sulphid, CoS, insoluble in cold, dilute Hydrochloric Acid, HCl, Acetic Acid, $HC_2H_3O_2$, and excess of Ammonium Sulphid, $(NH_4)_2S$. Soluble in Nitrohydrochloric Acid, and Nitric Acid, HNO_3, upon heating. Precipitation prevented by strong acids. Ammonium Chlorid, NH_4Cl, materially promotes precipitation.

295. Potassium and Sodium Hydroxids, KOH and NaOH, produce blue precipitates of a Basic Cobaltous salt. Upon boiling, the precipitate is converted into pink Cobaltous Hydroxid, $Co(OH)_2$. Upon exposure to air both precipitates become oxidized and turn brownish in color. They are insoluble in excess of the reagents. Soluble in acids, Ammonium Hydroxid, NH_4OH, and Ammonium Carbonate, $(NH_4)_2CO_3$.

296. Ammonium Hydroxid, NH_4OH, produces the same result as the foregoing, but the precipitate is soluble in an excess of the precipitant forming a reddish-colored fluid. Ammonium salts prevent precipitation.

297. Potassium Cyanid, KCN, produces a reddish-brown precipitate of Cobaltous Cyanid, $Co(CN)_2$, soluble in excess of the precipitant forming Potassium Cobaltocyanid, $K_4Co(CN)_6$. If the solution is boiled in contact with the air, it undergoes oxidation with the formation of Potassium Cobalticyanid, $K_3Co(CN)_6$, which is not decomposed by the addition of a Hypochlorite or a Hypobromite. (Difference from Nickel.)

298. Potassium Nitrite, KNO_2, added in excess to a solution of a Cobalt salt to which Acetic Acid, $HC_2H_3O_2$, has been added until strongly acid, produces a yellow, crystalline precipitate of Potassium Cobaltic Nitrite, $K_3Co(NO_2)_6$. In dilute solutions the precipitation takes place very slowly. The precipitate is soluble in water, but insoluble in the presence of the precipitant. When boiled with water, it dissolves forming a red fluid from which alkalies precipitate Cobaltous Hydroxid, $Co(OH)_2$.

299. Bromin Water, or a solution of Hydrogen Dioxid, H_2O_2, added to a solution of a Cobalt salt which has been treated with Potassium or Sodium Hydroxids, KOH and NaOH, and boiled, produce brownish-black precipitates of Cobaltic Hydroxid, $Co(OH)_3$, soluble in acids; sparingly soluble in Bromin Water, and in 2% KCN. Interfered with by Potassium Cyanid, KCN, which forms soluble $K_3Co(CN)_6$ or $Na_3Co(CN)_6$ (ion, $Co(CN)_6^{---}$).

300. Dry Cobalt compounds fused in a Borax Bead impart to it a sapphire-blue color.

NICKEL

Symbol, $Ni^{2+;3+}$. Atomic Weight, 58.68. Valence, II, III.

301. NICKEL is a lustrous, silver-white, hard, malleable metal. Melting Point, 1500°–1600°. S./G., 8.9.

A solution of Nickel Sulphate, $NiSO_4$, or Nickel Chlorid, $NiCl_2$, may be used for the following tests:

TESTS

302. Ammonium Sulphid, $(NH_4)_2S$, or Hydrogen Sulphid, H_2S, in neutral and alkaline solutions, produce black precipitates of Nickel Sulphid, NiS, soluble in Nitrohydrochloric Acid, and slightly so in Ammonium Poly-Sulphid, $(NH_4)_2S_x$. Insoluble in diluted Hydrochloric Acid, HCl, and Acetic Acid, $HC_2H_3O_2$. The presence of Ammonium Chlorid, NH_4Cl, considerably promotes precipitation.

303. Potassium and Sodium Hydroxids, KOH and NaOH, produce apple-green precipitates of Nickelous Hydroxid, $Ni(OH)_2$, insoluble in excess of the precipitants. Soluble in Ammonium Carbonate, $(NH_4)_2CO_3$, giving a greenish blue fluid. Also soluble in Hydrochloric, Nitric, and Sulphuric Acids, HCl, HNO_3, and H_2SO_4.

304. Ammonium Hydroxid, NH_4OH, added in small quantity, produces an apple-green precipitate of a basic salt, which dissolves in an excess of the precipitant forming a blue fluid ($Ni(NH_3)_6^{++}$).

305. Potassium Cyanid, KCN, produces a greenish precipitate of Nickel Cyanid, $Ni(CN)_2$, soluble in excess of the precipitant forming Potassium Nickelous Cyanid, $K_2Ni(CN)_4$. If this solution is made strongly alkaline with Potassium or Sodium Hydroxid, KOH or NaOH, and treated with a Hypochlorite or Hypobromite, a black precipitate of Nickelic Hydroxid, $Ni(OH)_3$, is formed.

306. Potassium Nitrite, KNO_2, with Acetic Acid, $HC_2H_3O_2$, does not produce a precipitate with Nickel compounds except in very concentrated solutions.

307. Bromin Water, or a solution of Sodium Hypochlorite, NaClO, added to a solution of a Nickel salt which has been treated with Potassium or Sodium Hydroxid, KOH or NaOH, and heated, produces a black precipitate of Nickelic Hydroxid, $Ni(OH)_3$, soluble in a mixture of Ammonium Hydroxid, NH_4OH; Ammonium Chlorid, NH_4Cl; slowly soluble in Bromin Water; more soluble in 2% KCN. From the latter it is readily reprecipitated by adding Sodium Carbonate, an excess of Bromin Water and heating. (Compare with Cobalt.)

308. Dry Nickel compounds fused in a Borax Bead in the oxidizing flame impart a reddish-brown color to the bead on cooling.

CHAPTER XI

Separation of Group 5

309. After separating Group 4, the following should be carried out either on the filtrate from Group 4, or a solution containing the members of Group 5.

310. If a simple solution of the members of Group 5 is to be used, Ammonium Chlorid and Ammonium Hydroxid must be added before the Hydrogen Sulphid is passed thru. If Group 4 has been tested for, more Ammonium Chlorid must not be added.

311. Warm the filtrate (or solution of the members of Group 5 to which Ammonium Chlorid has been added), add Ammonium Hydroxid, and pass in Hydrogen Sulphid until no further precipitation takes place by the continued passage of the reagent. *In order to insure the complete precipitation of the members of this Group,* filter a small amount of the fluid, and pass Hydrogen Sulphid into the filtrate. If a precipitate forms, return the mixture to the rest of the fluid and repeat the passing of the Hydrogen Sulphid until the desired result is secured.

312. Now heat the mixture until the precipitate settles out, filter, and wash the precipitate with a *weak* solution of Ammonium Sulphid. Save the filtrate (and washings) for Groups 6 and 7.

313. Transfer the precipitate to a dish by washing it off the paper with *cold,* 5% Hydrochloric Acid. Mix thoroughly by triturating with a pestle and let stand at least 5 minutes. Filter. Wash the precipitate with water containing Hydrogen Sulphid and set it aside.

314. Warm the Hydrochloric Acid filtrate until free from Hydrogen Sulphid, and then add Sodium Hydroxid in excess. A whitish precipitate, which upon exposure to air rapidly turns brown indicates MANGANESE. Filter off the precipitate and confirm the presence of Manganese by drying and fusing the precipitate with Sodium Carbonate and Potassium Nitrate; a blue-green mass confirms MANGANESE.

315. Next test the Sodium Hydroxid filtrate for Zinc by passing Hydrogen Sulphid thru it. A white precipitate indicates ZINC.

316. Returning to the precipitate insoluble in the cold, 5% Hydrochloric Acid which contains the Sulphids of Nickel and Cobalt. Test the precipitate in a borax bead by ¶300–308. A blue bead indicates COBALT. A reddish-brown bead indicates NICKEL, and shows the absence of more than traces of Cobalt. However, since the blue color of Cobalt may cover the reddish-brown of Nickel, the following separation must be carried out to *determine Nickel in the presence of Cobalt.*

317. Dissolve the precipitate (NiS and CoS) by heating with Nitro-hydrochloric Acid. Boil to drive off the greater part of the Hydrochloric Acid and Nitrosyl Chlorid, and then neutralize the solution by adding Sodium Hydroxid *drop by drop* until a permanent precipitate of Nickel and Cobalt Hydroxids is formed. Filter. Reject the filtrate. Dissolve the precipitate in Acetic Acid, concentrate by evaporation, then mix with 20% solution of Potassium Nitrite and allow it to stand for 24 hours. The Cobalt is precipitated as yellow, crystalline Potassium Cobaltic Nitrite ($K_3Co(NO_2)_6$). The Nickel remains in solution and can be detected by adding Sulphuric Acid to the filtrate from the above, boiling, cooling, and adding Sodium Hydroxid until alkaline. An apple-green precipitate indicates NICKEL, confirmed by the borax bead test on this washed precipitate.

COMMENTS

318. The filtrate from Group 4 contains the members of Groups 5, 6 and 7. Since Ammonium Chlorid has already been added in the precipitation of Group 4, it should not be added here. (If a simple solution of the members of this Group is used, Ammonium Chlorid must be added to prevent

TABLE VI.—Group 5 ($H_2S - NH_4OH$ Group)

Transfer group precipitate to dish with cold, 5% HCl. Triturate thoroughly and let stand for 5 minutes. Filter. (¶313)

(I) INSOLUBLE RESIDUE:—Wash with H_2S water and test in Borax Bead:— 1. If BLUE, indicates COBALT. 2. If REDDISH-BROWN, indicates NICKEL. (¶316.) If BLUE, Nickel may also be present. Therefore carry out separation described in ¶317.	(II) FILTRATE:—Warm till free from H_2S, add excess NaOH. Filter. (¶314.)	
	(1) PRECIPITATE:—A WHITISH precipitate ($Mn(OH)_2$) indicates MANGANESE. Confirm by fusion with Na_2CO_3 and KNO_3 gives a BLUE-GREEN mass (Na_2MnO_4 and K_2MnO_4). (¶314.)	(2) FILTRATE:—Pass H_2S thru. A WHITE precipitate (ZnS) indicates ZINC. (¶315.)

the precipitation of Magnesium as $Mg(OH)_2$ when Ammonium Hydroxid is added. See ¶ 265, page 102, Chapter IX.) The Ammonium Sulphid, $(NH_4)_2S$, formed when Hydrogen Sulphid is passed into the ammoniacal fluid completely precipitates the members of this Group. Warming assists precipitation. It is of the greatest importance that all the sulphids of this group be precipitated here. Therefore the precaution to insure a sufficient amount of Hydrogen Sulphid.

319. The precipitate of Group 5 is washed with a *weak* solution of Ammonium Sulphid to prevent the Manganese Sulphate from passing into colloidal solution and to prevent oxidation of the precipitate by the air. The filtrate, containing the members of Groups 6 and 7, is reserved for the separation of these Groups.

320. The treatment of the Group 5 precipitate with cold, 5% Hydrochloric Acid serves to dissolve the Manganese and Zinc Sulphids, while the Nickel and Cobalt remain undissolved. It is very important that the Manganese and Zinc be completely removed from the sulphids of

Nickel and Cobalt. Therefore, the thorough trituration to insure the breaking up of any lumps of precipitate. Filtration of this acid mixture separates the undissolved Nickel and Cobalt Sulphids from the solution containing the Manganese and Zinc.

321. After completely ridding the filtrate of Hydrogen Sulphid by warming, Sodium Hydroxid in excess precipitates the Manganese as whitish $Mn(OH)_2$, which on exposure to air rapidly oxidizes to brown $Mn(OH)_3$. The Zinc, at first precipitated as $Zn(OH)_2$, is dissolved by the excess of Sodium Hydroxid as Zincate (Na_2ZnO_2). Filtering removes the Manganese, which is confirmed by the fusion test (Na_2MnO_4 and K_2MnO_4 being formed). The alkaline filtrate is treated with Hydrogen Sulphid which precipitates white Zinc Sulphid.

322. The residue insoluble in cold, 5% Hydrochloric Acid is tested by the borax bead test for Nickel and Cobalt, In the presence of a *blue* bead, the separation of Cobalt and Nickel must be carried out.

CHAPTER XII

Group 6

Metals or Cations precipitated as Carbonates by Ammonium Carbonate.

BARIUM

Symbol, Ba^{++}. Atomic Weight, 137.37. Valence, II.

323. BARIUM is a yellowish-white metal. Melting Point 850°C. S./G., 3.75.

A solution of Barium Chlorid, $BaCl_2$, may be used for the following tests:

TESTS

324. Soluble carbonates like Ammonium Carbonate, $(NH_4)_2CO_3$, produce white precipitates of Barium Carbonate, $BaCO_3$. If the solution is acid, complete precipitation takes place only after heating. The precipitate is easily soluble in diluted Hydrochloric Acid, HCl, in Nitric Acid, HNO_3 and Acetic Acid, $HC_2H_3O_2$. Soluble in excess of Ammonium Chlorid, NH_4Cl, upon boiling.

325. Sulphuric Acid, H_2SO_4, and soluble sulphates produce fine, white precipitates of Barium Sulphate, $BaSO_4$, insoluble in alkalis, nearly insoluble in diluted acids. Very slightly soluble in strong, hot Hydrochloric Acid, HCl, and Nitric Acid, HNO_3.

326. Ammonium Oxalate, $(NH_4)_2C_2O_4$, produces a white precipitate of Barium Oxalate, $BaC_2O_4.H_2O$; soluble in Nitric Acid, HNO_3, and Hydrochloric Acid, HCl. Readily dissolved by hot dilute Acetic Acid, $HC_2H_3O_2$.

327. Potassium Chromate, K_2CrO_4, produces a bright yellow precipitate of Barium Chromate, $BaCrO_4$, soluble in

Hydrochloric Acid, HCl, and Nitric Acid, HNO_3. Soluble in Acetic Acid, $HC_2H_3O_2$.

328. Di-sodium Hydrogen Phosphate, Na_2HPO_4, produces a white precipitate of Barium Hydrogen Phosphate, $BaHPO_4$, soluble in Nitric Acid, HNO_3; Hydrochloric Acid, HCl; and Acetic Acid, $HC_2H_3O_2$.

329. Sodium Hydroxid, NaOH, and Potassium Hydroxid, KOH, produce, in very concentrated solutions only, white precipitates of Barium Hydroxid, $Ba(OH)_2$, which redissolve in water.

330. Barium Compounds, heated on a Platinum wire in the colorless flame of a Bunsen burner, impart a yellowish-green color to the flame.

CALCIUM

Symbol, Ca^{++}. Atomic Weight, 40.07. Valence, II.

331. CALCIUM is a white, lustrous, tough, malleable metal. Melting Point, 760°C. S./G., 1.83.

A solution of Calcium Chlorid, $CaCl_2$, may be used for the following tests:

TESTS

332. Soluble carbonates like Ammonium Carbonate, $(NH_4)_2CO_3$, produce white precipitates of Calcium Carbonate, $CaCO_3$, easily soluble in diluted Hydrochloric Acid, HCl; in Nitric Acid, HNO_3, and Acetic Acid, $HC_2H_3O_2$. Soluble in excess of Ammonium Chlorid, NH_4Cl, upon boiling.

333. Sulphuric Acid, H_2SO_4, and soluble sulphates produce white precipitates of Calcium Sulphate, $CaSO_4$; soluble in hot Hydrochloric Acid, HCl. Insoluble in Alcohol, C_2H_5OH. In dilute solution precipitation takes place very slowly or not at all.

334. Ammonium Oxalate, $(NH_4)_2C_2O_4$, produces a white crystalline precipitate of Calcium Oxalate, $CaC_2O_4.H_2O$, soluble in Hydrochloric and Nitric Acid, HCl and HNO_3; insoluble in Acetic Acid, $HC_2H_3O_2$, and Oxalic Acid, $H_2C_2O_4$.

335. Potassium Chromate, K_2CrO_4, does not produce a precipitate in dilute solutions. Strong, neutral solutions are very slowly precipitated.

336. Di-sodium Hydrogen Phosphate, Na_2HPO_4, produces a white precipitate of Calcium Hydrogen Phosphate, $CaHPO_4$, soluble in Hydrochloric, Nitric and Acetic Acids, HCl, HNO_3 and $HC_2H_3O_2$.

337. Sodium Hydroxid, $NaOH$, and Potassium Hydroxid, KOH, in very concentrated solutions, produce white precipitates of Calcium Hydroxid, $Ca(OH)_2$, soluble in water. Solution becomes turbid upon heating, but clears somewhat upon cooling.

338. Calcium Compounds, heated on a Platinum wire in the colorless flame of a Bunsen burner, impart a reddish-yellow color to the flame.

STRONTIUM

Symbol, Sr^{++}. Atomic Weight, 87.63. Valence, II.

339. STRONTIUM is a yellowish, tough metal. Melts at low red heat. S./G., 2.5.

A solution of Strontium Nitrate, $Sr(NO_3)_2$, or Strontium Chlorid, $SrCl_2$, may be used for the following tests.

TESTS

340. Soluble carbonates like Ammonium Carbonate, $(NH_4)_2CO_3$, produce white precipitates of Strontium Carbonate, $SrCO_3$, soluble in diluted Hydrochloric Acid, HCl, in Nitric Acid, HNO_3, and Acetic Acid, $HC_2H_3O_2$. Soluble in Ammonium Chlorid, NH_4Cl, upon boiling.

341. Sulphuric Acid, H_2SO_4, and soluble sulphates, including Calcium Sulphate, $CaSO_4$, produce white precipitates of Strontium Sulphate, $SrSO_4$. Heat assists precipitation. Soluble to a slight extent in Hydrochloric Acid, HCl, and Nitric Acid, HNO_3. Insoluble in Alcohol, C_2H_5OH, and Ammonium Sulphate, $(NH_4)_2SO_4$.

342. Ammonium Oxalate, $(NH_4)_2C_2O_4$, produces a white precipitate of Strontium Oxalate, $2SrC_2O_4.5H_2O$, soluble in Hydrochloric and Nitric Acids, HCl and HNO_3. Somewhat soluble in Acetic Acid, $HC_2H_3O_2$.

343. Potassium Chromate, K_2CrO_4, in concentrated solutions only, produces a yellow precipitate of Strontium Chromate, $SrCrO_4$, soluble in Hydrochloric Acid, HCl, and Nitric Acid, HNO_3. Solutions containing Acetic Acid, $HC_2H_3O_2$, do not yield a precipitate with the reagent.

344. Di-sodium Hydrogen Phosphate, Na_2HPO_4, produces a white precipitate of Strontium Hydrogen Phosphate, $SrHPO_4$, soluble in Hydrochloric, Nitric and Acetic Acids, HCl, HNO_3 and $HC_2H_3O_2$.

345. Sodium Hydroxid, NaOH, and Potassium Hydroxid, KOH, produce white precipitates of Strontium Hydroxid, $Sr(OH)_2$, in very concentrated solutions. Precipitate is soluble in water.

346. Strontium Compounds, heated on a Platinum wire in the colorless flame of a Bunsen burner, impart a crimson color to the flame.

CHAPTER XIII

Separation of Group 6

347. The members of Group 6 are precipitated from warm solution, neutral or alkaline, as insoluble Carbonates by adding Ammonium Carbonate in slight excess.

348. If the filtrate from the precipitate of Group 5, or a solution free from the members of the first five groups is used for the analysis of Groups 6 and 7, the following method may be employed to advantage instead of precipitating the group directly from the filtrate.

349. Evaporate the filtrate, or solution free from the first five groups, to dryness in a porcelain dish, and heat the residue strongly to expell the ammonium salts present. Dissolve the residue in water with the aid of a little Hydrochloric Acid, using enough water to make the bulk of the solution about three quarters of the original bulk. Filter.

350. Add to the filtrate an amount of Ammonium Chlorid solution equal to about one quarter of the volume of the filtrate, then Ammonium Hydroxid until alkaline, and finally Ammonium Carbonate in slight excess.

351. After thoroughly shaking, warm the mixture, allow it to stand a short time and filter. The filtrate should be tested with a little more Ammonium Carbonate in order to insure that all of the members of Group 6 are precipitated completely. Save the filtrate for Group 7.

352. The precipitate which forms in the presence of members of Group 6, consists of Barium, Strontium and Calcium Carbonates, while the filtrate contains the members of Group 7, if present.

353. Dissolve the Group precipitate, after washing, in as little warm diluted Acetic Acid as is necessary, by pouring and repouring the acid over the precipitate on the filter paper. After the precipitate is completely dissolved, wash the filter with a little warm water, collecting the wash water in the tube containing the acid filtrate.

354. Test a small portion of this acid liquid for Barium by adding to it a few drops of Potassium Chromate. The formation of a yellow precipitate indicates the presence of BARIUM. If a yellow precipitate is not formed, Barium is absent and the remainder of the liquid is examined directly for Calcium and Strontium. (¶358–360.)

355. If Barium is found by the above test, the remainder of the acid liquid is treated with Potassium Chromate in excess and boiled. The precipitated Barium Chromate is removed by filtration and rejected.

356. The filtrate, containing the Calcium and Strontium, is made alkaline with Ammonium Hydroxid, and is then warmed with an excess of Ammonium Carbonate. This reprecipitates the Calcium and Strontium, as carbonates. Filter and reject the filtrate.

357. After washing the precipitate thoroughly with water, dissolve it in as little Acetic Acid as is necessary, in the same manner as described above. The acid liquid contains the Calcium and Strontium as acetates.

358. To separate the Strontium from the Calcium, evaporate the acid solution to small bulk, and then add from 20 to 25 Cc. of a solution of Potassium Sulphate (1–200). Insure the addition of a sufficient quantity of the sulphate solution by allowing the mixture to stand for from 20 to 30 minutes, and then testing a small portion of the clear supernatant liquid with a little more Potassium Sulphate solution. If a precipitate forms in this, add Potassium Sulphate solution to the remainder of the mixture. The formation of a fine white precipitate by the above treatment indicates the presence of STRONTIUM.

359. To confirm Strontium, filter the mixture, set the filtrate, which contains the Calcium, aside, and wash the precipitate on the paper thoroughly with water. Add a *few* *drops* of Hydrochloric Acid to the precipitate, dip a clean Platinum wire into the mixture, and hold the wire in the colorless flame of a Bunsen burner. A lasting, deep crimson flame confirms STRONTIUM.

360. To detect Calcium in the liquid from which Strontium has been precipitated by Potassium Sulphate, add sufficient Ammonium Hydroxid to make the liquid alkaline, and 2 or 3 Cc. of Ammonium Oxalate solution. The formation of a fine white precipitate indicates the presence of CALCIUM.

COMMENTS

361. The solution containing the members of Group 6 is first treated with one quarter volume of Ammonium Chlorid, then with Ammonium Hydroxid until alkaline, and finally warmed with Ammonium Carbonate in order to precipitate them, since they form insoluble carbonates with Ammonium Carbonate in alkaline solution.

362. If the filtrate from Group 5 is used, the addition of Ammonium Chlorid may be omitted since it has already been added in the precipitation of Group 5.

363. The Ammonium Carbonate is added as long as a precipitate forms. To insure the addition of an excess, the filtrate is tested with a small amount of the reagent. Too large an excess of Ammonium Carbonate must be avoided, since a large excess of the reagent would remain in the filtrate and interfere, to some extent, with the tests for Magnesium, Potassium, Sodium and Lithium which are made on this filtrate. Therefore, if the addition of Ammonium Carbonate to a small amount of the filtrate shows the absence of Barium, Strontium and Calcium, it is unnecessary to add the reagent to the rest of the liquid.

364. The addition of Ammonium Chlorid, altho a disadvantage as far as the precipitation of Group 6 is concerned (since their Carbonates are slightly soluble in excess of Ammonium Chlorid), is necessary in order to prevent the precipitation of Magnesium as Magnesium Carbonate.

365. If the analysis of an unknown substance is being carried out, the student will find less difficulty in precipitating the Carbonates of this Group, especially if present in small amounts, by evaporating the filtrate from Group 5 as directed in the Separation, instead of precipitating directly from the filtrate. The strong heating of the residue by this method destroys the Ammonium salts and Sulphur it contains, as these substances interfere somewhat with the delicacy of the tests for Barium, Strontium and Calcium. The treatment described may render the Barium, Strontium and Calcium compounds partly insoluble, but this is overcome by using a little Hydrochloric Acid in dissolving the residue left after evaporation.

366. After the evaporation and solution processes are carried out, the Ammonium Chlorid, Ammonium Hydroxid and Ammonium Carbonate are added for the reasons given above. The mixture is warmed to prevent the formation of soluble Bicarbonates.

367. The group precipitate obtained consists, as already stated, of the Carbonates of Barium, Strontium and Calcium. The members of Group 7, being uneffected by the treatment, are found in the filtrate.

368. After washing the precipitate, warm diluted Acetic Acid is used to dissolve it. An excess of the acid is avoided.

369. Barium is tested for on a portion of the acid solution by adding drop by drop some solution of Potassium Chromate which will produce a yellow precipitate of Barium Chromate if Barium is present.

370. If Barium is found, the rest of the solution is then treated with Potassium Chromate solution added in drops, and thoroughly shaken after each addition, as long as a precipitate forms. Boiling aids the complete precipitation of all the Barium present.

371. If Barium is not found by the test made on a portion of the solution, the addition of Potassium Chromate to the rest of the solution is omitted, and the solution is tested directly for Calcium and Strontium.

372. The filtrate contains only the Strontium and Calcium, which are separated and identified by making the solu-

TABLE VII.—GROUP 6 ($(NH_4)_2CO_3$ Group)

Dissolve the Group Precipitate in a small am't of warm, diluted $HC_2H_3O_2$. To a small portion add K_2CrO_4. A YELLOW precipitate ($BaCrO_4$) indicates BARIUM. *If BARIUM is found,* treat the remainder of the acid liquid with K_2CrO_4 in excess and boil. Filter. (¶353–355.) (If Barium is *not* found, test the liquid directly for Strontium and Calcium as per ¶358–360.)		
(1) PRECIPITATE:—Is $BaCrO_4$. Reject. (¶355.)		
(II) FILTRATE:—Add NH_4OH until alkaline. Then add an excess of $(NH_4)_2CO_3$ and warm. Filter. (¶356.)		
(I) PRECIPITATE:—Wash. Dissolve in small am't of warm $HC_2H_3O_2$. Evaporate to small bulk. Add K_2SO_4 (1-200) in excess. Let stand ½ hour. Test supernatant liquid with K_2SO_4. Filter. (¶357–358.)		(2) FILTRATE:—Reject. (¶356.)
(A) PRECIPITATE:—A fine WHITE precipitate ($SrSO_4$) indicates STRONTIUM. To confirm: Wash. Dissolve in few drops HCl and test on Pt wire in flame. A *lasting* DEEP CRIMSON flame indicates STRONTIUM. (¶358–359.)	(B) FILTRATE:—Add NH_4OH until alkaline. Then add $(NH_4)_2C_2O_4$. A fine WHITE precipitate (CaC_2O_4) indicates CALCIUM. (¶360.)	

tion alkaline with Ammonium Hydroxid and then warming with Ammonium Carbonate. They are reprecipitated in order to get rid of the excess of the chromate solution used in the precipitation of Barium.

373. The precipitated Strontium and Calcium Carbonates are dissolved in warm diluted Acetic Acid as above. Strontium is then precipitated as Strontium Sulphate by means of a very dilute Solution of Potassium Sulphate. The washed precipitate of Strontium Sulphate is mixed with a few drops of Hydrochloric Acid and tested on a Platinum wire in the Bunsen flame.

374. The filtrate, containing the Calcium, is treated with Ammonium Hydroxid until alkaline, and then with Ammonium Oxalate, which produces a fine, white precipitate of Calcium Oxalate in the presence of Calcium.

CHAPTER XIV

Group 7

Metals or Cations not precipitated by any one Group Reagent.

POTASSIUM (KALIUM)

Symbol, K^+. Atomic Weight, 39.1. Valence, I.

375. POTASSIUM is a soft, waxy, silver-white metal. Melting Point, 62.5°C. S./G., 0.865.

A solution of Potassium Nitrate, KNO_3, or Potassium Chlorid, KCl, may be used for the following tests:

TESTS

376. Chloroplatinic Acid, H_2PtCl_6, in concentrated solutions of the Chlorid, produces a yellow, crystalline precipitate of Potassium Chloroplatinate, K_2PtCl_6, slightly soluble in water. Insoluble in Alcohol, C_2H_5OH. Precipitation is assisted by the addition of Alcohol and stirring.

377. Sodium Hydrogen Tartrate, $NaHC_4H_4O_6$, and Tartaric Acid, $H_2C_4H_4O_6$, in concentrated solutions, produce white crystalline precipitates of Potassium Hydrogen Tartrate or "Cream of Tartar," $KHC_4H_4O_6$. Precipitation assisted by stirring and the addition of Alcohol, C_2H_5OH.

378. Perchloric Acid, $HClO_4$, produces a white crystalline precipitate of Potassium Perchlorate, $KClO_4$.

379. Sodium Cobaltic Nitrite, $Na_3Co(NO_2)_6$, produces a yellow, crystalline precipitate of Potassium Cobaltic Nitrite, $K_3Co(NO_2)_6$, from neutral or alkaline solutions.

380. Potassium Compounds impart a violet color to the colorless flame of a Bunsen burner. Since traces of Sodium obscure this reaction, it is best viewed thru a piece of Cobalt glass, which absorbs the light emitted by Sodium Compounds.

SODIUM (NATRIUM)

Symbol, Na^+. Atomic Weight, 23. Valence, I.

381. SODIUM is a soft, waxy, silver-white metal. Melting Point, 95.6°C. S./G., 0.9735.

A solution of Sodium Chlorid, NaCl, may be used for the following tests:

TESTS

382. Chloroplatinic Acid, H_2PtCl_6, does not produce a precipitate.

383. Sodium Hydrogen Tartrate, $NaHC_4H_4O_6$, does not produce a precipitate.

384. Tartaric Acid, $H_2C_4H_4O_6$, does not produce a precipitate.

385. Potassium Pyroantimoniate, $K_2H_2Sb_2O_7$, in neutral or slightly alkaline solutions, produces a white, crystalline precipitate of Sodium Pyroantimoniate, $Na_2H_2Sb_2O_7 . 6H_2O$. This test is inapplicable in the presence of metals other than Potassium, as they precipitate the Potassium Pyroantimoniate.

386. Compounds of Sodium impart an intense yellow color to the colorless flame of the Bunsen burner.

MAGNESIUM

Symbol, Mg^{++}. Atomic Weight, 24.32. Valence, II.

387. MAGNESIUM is a white, hard, malleable, strongly lustrous metal. Melting Point, about 750°C. S./G., 1.75.

A solution of Magnesium Sulphate, $MgSO_4$, may be used for the following tests:

TESTS

388. Di-sodium Hydrogen Phosphate, Na_2HPO_4, in concentrated solutions, produces a white, flocculent precipitate of Magnesium Hydrogen Phosphate, $MgHPO_4$. If Ammonium Chlorid, NH_4Cl, and Ammonium Hydroxid, NH_4OH, are added before the addition of the Sodium Hydrogen Phosphate, a white crystalline precipitate of Magnesium Ammonium Phosphate, $MgNH_4PO_4.6H_2O$, is formed. Stirring assists precipitation from dilute solutions. The precipitate is soluble in Hydrochloric, Nitric and Acetic Acids, HCl, HNO_3 and $HC_2H_3O_2$.

389. Ammonium Carbonate, $(NH_4)_2CO_3$, produces a white precipitate of Basic Magnesium Carbonate, $3MgCO_3.Mg(OH)_2$, on boiling, in solutions free from Ammonium salts. In dilute solutions this precipitate may appear only after long standing. In excess of Ammonium Carbonate, a white crystalline precipitate of $MgCO_3(NH_4)_2CO_3$ is formed. Large quantities of Ammonium salts prevent precipitation.

390. Sodium Carbonate, Na_2CO_3, and Potassium Carbonate, K_2CO_3, produce white precipitates of Basic Magnesium Carbonate, $3MgCO_3.Mg(OH)_2$, soluble in Ammonium Chlorid, NH_4Cl.

391. Ammonium Hydroxid, NH_4OH, produces a white, flocculent precipitate of Magnesium Hydroxid, $Mg(OH)_2$. Precipitation is incomplete, and does not take place in the presence of Ammonium salts. Ammonium Hydroxid in the presence of a high concentration of Ammonium ion is a much weaker base than Magnesium Hydroxid, and therefore if an Ammonium salt, like Ammonium Chlorid, NH_4Cl, is added to a solution containing Magnesium Hydroxid, the Hydroxyl ion from the $Mg(OH)_2$ will combine with the Ammonium ion to form the slightly dissociated Ammonium Hydroxid, thus decreasing the amount of Magnesium Hydroxid in solution. Therefore, the addition of Ammonium salts readily dissolves the precipitate of Magnesium Hydroxid.

392. Potassium and Sodium Hydroxids, KOH and $NaOH$, produce white precipitates of Magnesium Hydroxid, $Mg(OH)_2$. Precipitation is assisted by boiling.

393. Magnesium Compounds do not impart a color to the colorless flame of the Bunsen burner.

LITHIUM

Symbol, Li^+. Atomic Weight, 6.94. Valence, I.

394. LITHIUM is a silver-white, ductile metal. Melting Point, 180°C. S./G., 0.59.

A solution of Lithium Chlorid, $LiCl$, may be used for the following tests.

TESTS

395. Di-sodium Hydrogen Phosphate, Na_2HPO_4, in concentrated solutions, produces a white, crystalline precipitate of Lithium Phosphate, Li_3PO_4.

396. Sodium Carbonate, Na_2CO_3, produces in cold concentrated solutions a white precipitate of Lithium Carbonate, Li_2CO_3.

397. Lithium Compounds impart a carmine-red color to the colorless flame of the Bunsen burner.

AMMONIUM

Formula, NH_4^+. Molecular Weight, 18.042. Valence, I.

398. The cation Ammonium, NH_4, does not exist in the free state, but corresponds in its behavior with anions to Potassium and Sodium. It also forms an amalgam.

A solution of Ammonium Chlorid, NH_4Cl, may be used for the following tests:

TESTS

399. Chloroplatinic Acid, H_2PtCl_6, in concentrated solutions, produces a yellow, crystalline precipitate of Ammonium Chloroplatinate, $(NH_4)_2PtCl_6$, similar in appearance to the corresponding Potassium salt. The precipitate is soluble in water, but insoluble in Alcohol, C_2H_5OH. Stirring and the addition of Alcohol assists precipitation.

400. Sodium Hydrogen Tartrate, $NaHC_4H_4O_6$, in concentrated solutions, produces a white, crystalline precipitate of Ammonium Hydrogen Tartrate, $NH_4HC_4H_4O_6$. Precipitation assisted by stirring. The precipitate is soluble in acids and alkali hydroxids.

401. Tartaric Acid, $H_2C_4H_4O_6$, under the same conditions, produces the same precipitate.

402. Sodium Cobaltic Nitrite, $Na_3Co(NO_2)_6$, produces a precipitate similar to that produced in solutions of Potassium salts. The precipitate formed is Ammonium Cobaltic Nitrite, $(NH_4)_3Co(NO_2)_6$.

403. Potassium and Sodium Hydroxids, KOH and NaOH, added to a solution of an Ammonium compound, liberate Ammonia gas, NH_3, on boiling. The gas may be detected by its odor or by the color it imparts to red litmus.

404. Nessler's Reagent ($HgI_2.2KI$ or K_2HgI_4) produces a brownish precipitate, or, if the solution is very dilute, a yellowish-brown color. The compound produced has the formula NH_2-Hg_2OI. The reaction is an extremely delicate one, for by it, one part of Ammonia in one million parts of water can be easily detected.

CHAPTER XV

Separation of Group 7

405. A solution containing the members of this Group, or the filtrate from the precipitate of Group 6 in the case of unknown solutions, is examined as follows:

406. If the filtrate from the precipitate of Group 6 is being examined, it will contain not only the members of Group 7, but, in addition, some of the reagents used to precipitate the members of the preceding Groups. Ammonium compounds, which were used to precipitate other Groups will be present, and this filtrate can not be used for the detection of Ammonium Compounds which may have been in the original substance.

407. A portion of the original material is therefore tested for Ammonium Compounds as follows: Add a solution of Potassium Hydroxid or Sodium Hydroxid until alkaline and boil. Close the mouth of the tube with the thumb. If Ammonium Compounds are present Ammonia gas will be evolved, and may be recognized by its odor, or by its effect on moistened red litmus paper which is turned blue. If litmus paper is used, care must be taken that the paper does not come in contact with the sides of the tube, in which case the paper may be turned blue by the alkali hydroxid which may be on the sides of the tube.

408. If a solution containing ONLY members of Group 7 is being examined, the test for Ammonium Compounds is of course made on a portion of it.

409. Divide the filtrate, or solution, into a large and a small portion. The *small* part of the filtrate, or solution, containing the members of Group 7 is examined for Magnesium. Add to it Ammonium Chlorid and Ammonium Hydroxid, if not already present, and some Di-sodium Hydrogen Phosphate solution. If MAGNESIUM is present, a white, crystalline precipitate of Magnesium Ammonium Phosphate will appear at once, or, in the case of dilute solutions, after standing some time. If the precipitate is other than crystalline, Magnesium is absent.

410. If Magnesium is not found by the foregoing test, the rest of the liquid is evaporated to dryness, as directed below, and the residue tested directly for Lithium, etc. (¶415–423.)

411. If Magnesium is found, evaporate the large part of the filtrate, or solution, to dryness on a water-bath, and carefully heat the residue over the free flame until the white fumes of the Ammonium salts cease to be evolved.

412. If no residue remains, Potassium, Sodium and Lithium are absent.

413. In the case of a residue, dissolve it in water and a few drops of Hydrochloric Acid. Boil the fluid and add Barium Hydroxid. This will precipitate all of the Magnesium as Magnesium Hydroxid. Filter off the precipitate and reject it.

414. Add Ammonium Carbonate to the filtrate to precipitate the Barium as insoluble Barium Carbonate. Filter again and reject the precipitate.

415. Evaporate the filtrate to dryness and gently ignite the residue until free from Ammonium salts as above.

416. Test the residue for Lithium by means of the flame test. A carmine color imparted to the nonluminous flame of the Bunsen burner indicates LITHIUM.

417. If Lithium is absent, dissolve the remainder of the residue in the smallest possible quantity of water and test for Sodium and Potassium as described in ¶421, 422, 423.

418. If Lithium is found by the flame test, to confirm, moisten the residue with concentrated Hydrochloric Acid and evaporate to dryness on a water-bath.

419. Extract this residue with a mixture of equal parts of absolute Alcohol and Ether. Lithium Chlorid dissolves leaving the Potassium and Sodium Chlorids as insoluble residue. Filter.

420. Evaporate the filtrate to dryness on a water-bath, place a portion of the residue on a Platinum wire, and hold it in the non-luminous flame. LITHIUM, if present, will impart a carmine color to the flame.

421. Dissolve the residue, insoluble in the mixture of Alcohol and Ether, in the smallest possible quantity of water and filter thru a very small filter. Moisten a clean Platinum wire with some of the filtrate, and hold in the non-luminous flame. An intense yellow flame indicates the presence of SODIUM. A violet flame indicates the presence of Potassium and the absence of Sodium.

422. If Sodium is found by the flame test, Potassium may also be present, since the violet color imparted by Potassium may be covered by the intense yellow color of the Sodium flame. To detect the Potassium flame in the presence of Sodium, a piece of Cobalt glass may be employed as in the special tests for Potassium. The blue glass cuts off the yellow rays and the violet can then be seen.

423. In order to *prove* the presence of Potassium, place a small quantity of the filtrate in a watch-glass, add a few drops of Alcohol and a small quantity of Chloroplatinic Acid, and stir with a glass rod. If Potassium is present, a yellow crystalline precipitate will form. It must be remembered that if all Ammonium salts are not driven off they will give the same colored precipitate with Chloroplatinic Acid as the Potassium salts.

COMMENTS

424. The test for Ammonium Compounds made on a portion of the original material depends upon the fact that Ammonium salts are decomposed, when heated with alkali hydroxids, yielding Ammonia gas.

425. A part of the alkaline filtrate from Group 6, or the fluid to which Ammonium Chlorid and Ammonium Hydroxid have been added, if not already present, is treated with Sodium Hydrogen Phosphate which precipitates Magnesium as white, crystalline Magnesium Ammonium Phosphate. The Ammonium Chlorid was added to prevent the precipitation of Magnesium as Magnesium Hydroxid first formed by the Ammonium Hydroxid. (See ¶265, page 102.)

426. The remainder of the liquid is evaporated to dryness and ignited to get rid of the large quantity of Ammonium salts which has been added in the separation of the members of the preceding groups, since these Ammonium salts interfere with the test for Potassium. Since all Ammonium salts are volatile, the method described removes them without interfering with the non-volatile Potassium, Sodium and Lithium compounds possibly present.

427. The residue is dissolved in water with the aid of Hydrochloric Acid, and the Magnesium removed before testing for Potassium, Sodium and Lithium. This is accomplished, as described, by precipitating Magnesium as insoluble Magnesium Hydroxid by boiling with Barium Hydroxid. The precipitated Magnesium Hydroxid is filtered off, and the Barium removed by precipitating it as insoluble Carbonate by the addition of Ammonium Carbonate. Filtration removes the Barium Carbonate, and the filtrate is freed from Ammonium compounds by heating as before.

428. Lithium is tested for in the residue by means of the Platinum wire. If found, the residue is moistened with Hydrochloric Acid to convert the three metals to chlorids.

429. This mixture of Potassium, Sodium and Lithium Chlorids is evaporated to dryness and Lithium (the only one of the three that is soluble in a mixture of Alcohol and Ether) removed by treatment with equal parts of Alcohol and Ether.

430. Upon filtering, the Potassium Chlorid and Sodium Chlorid remain on the filter, while the Lithium Chlorid passes thru in the filtrate.

431. The residue (KCl and $NaCl$), insoluble in Alcohol and Ether, is dissolved in a very small amount of water, filtered, and tested for Potassium and Sodium by the flame tests. Sodium if present would obscure the violet of the Potassium flame and therefore Cobalt glass is used to cut

TABLE VIII.—Group 7 (Alkali Group)

Divide the Filtrate from Group 6 (or solution free from all preceding Groups) into one small and one large portion. (¶409.)

(I) SMALL PART:—Add NH_4Cl, NH_4OH (*if not already present*) and Na_2HPO_4.
A WHITE, *crystalline* precipitate ($MgNH_4PO_4$) indicates MAGNESIUM.
If the precipitate is other than crystalline, Magnesium is absent. (¶409–410.) In either case reject.

(II) LARGE PART:—Evap. to dryness. Ignite until all white fumes cease to be evolved.
(*a*) If *no* residue remains, POTASSIUM, SODIUM and LITHIUM are absent. (¶412.)
(*b*) If a residue remains, dissolve in water with a few drops of HCl. Boil and add $Ba(OH)_2$. Filter. (¶411–413.)

(1) PRECIPITATE:—A white precipitate is $Mg(OH)_2$. Reject. (¶413.)

(2) FILTRATE:—Add $(NH_4)_2CO_3$ and filter. (¶414.)

(A) PRECIPITATE:—The precipitate is $BaCO_3$. Reject. (¶414.)

(B) FILTRATE:—Evap. to dryness and ignite till white fumes cease. (¶415) Test the residue on Pt wire in flame. A CARMINE flame indicates LITHIUM. (¶416.)
(*a*) If Lithium is *not* found (¶417), dissolve in few drops of water and test directly for Potassium and Sodium. (¶421–423.)
(*b*) If Lithium is found, moisten residue with concentrated HCl and evap. to dryness. Extract with mixture of absolute C_2H_5OH and $(C_2H_5)_2O$. Filter. (¶418–419.)

(*a*) RESIDUE:—Dissolve in very small am't of water. Filter. Test filtrate on Pt wire in flame. (*a*) A YELLOW flame indicates SODIUM. (*b*) A VIOLET flame indicates POTASSIUM. Note.—If YELLOW, Potassium *may* also be present. Therefore observe flame thru Co glass. A VIOLET color indicates POTASSIUM. To prove: Add to small am't of filtrate a few drops of C_2H_5OH and H_2PtCl_6. A YELLOW precipitate (K_2PtCl_6) indicates POTASSIUM. (¶421–423.)

(*b*) FILTRATE:—Evap. to dryness. Test residue on Pt wire. A CARMINE color indicates LITHIUM. (¶420.)

Note.—AMMONIUM compounds *must* be looked for in the original solution before the addition of any reagents. Therefore add KOH until alkaline and boil. An odor of NH_3 indicates AMMONIUM compounds. (¶407.)

off the yellow rays and reveal the violet color of Potassium. However, the Chloroplatinic Acid test should always be employed to confirm the presence of Potassium. Potassium Chloroplatinate is precipitated. (¶378 may also be used.)

432. Chloroplatinic Acid gives with Ammonium Compounds a fine, yellow precipitate of Ammonium Chloroplatinate, which it is practically impossible to distinguish by its appearance from Potassium Chloroplatinate. Ammonium Chloroplatinate, however, upon ignition leaves *only* metallic Platinum. It is very important therefore to expel all Ammonium salts before testing for Potassium with Chloroplatinic Acid. The heating process employed to drive off Ammonium salts does not effect the non-volatile Lithium, Sodium and Potassium compounds.

PART II

THE ACIDS OR ANIONS

433. It is essential that the student be familiar with the individual reactions of each Acid (as well as the reactions of each Metal already described and studied) before he can hope for success in testing complex mixtures. The Acids or Anions cannot be separated into Groups by a scheme of separation similar to that used for the Metals or Cations. They can be divided into Groups according to their reactions with reagents, but no successful method can be used for the detection of the individual members of these Groups by first precipitating a group and then attempting to isolate each constituent of this group precipitate. The Acids are therefore detected more by the application of the special tests described in the Chapters that follow.

434. For convenience they are divided into the following Groups:

Group A

Acids or Anions precipitated from neutral solution by BARIUM CHLORID.

Group B

Acids or Anions precipitated from dilute Nitric Acid solution by SILVER NITRATE.

Group C

Acids or Anions not precipitated by BARIUM CHLORID OR SILVER NITRATE.

CHAPTER XVI

Group A

435. Acids or Anions precipitated from neutral solution by BARIUM CHLORID.

In this Group are found Sulphates, Sulphites, Thiosulphates, Phosphates (Ortho, Pyro and Meta), Borates, Fluorids, Silicates, Carbonates, Chromates, Arsenates, Arsenites, and also the organic acids—Oxalates, Tartrates and Citrates.

SULPHURIC ACID AND SULPHATES

Formula, H_2SO_4. Anion, SO_4^{--}, and HSO_4^{-}.

436. Pure SULPHURIC ACID is a colorless, odorless, oily, heavy liquid, S./G., 1.84 (96 %).

Most of the sulphates are soluble in water, the most important exception being Barium. Those of Calcium, Strontium, and Lead are difficultly soluble. The anions SO_4^{--} and HSO_4^{--} are colorless and permanent.

A solution of Magnesium Sulphate, $MgSO_4$, may be used for the following tests:

TESTS

437. Barium Chlorid, $BaCl_2$, produces a white precipitate of Barium Sulphate, $BaSO_4$. The precipitate is insoluble in acids.

438. Lead Acetate, $Pb(C_2H_3O_2)_2$, produces a white precipitate of Lead Sulphate, $PbSO_4$, soluble in boiling concentrated acids, Ammonium Acetate, $NH_4C_2H_3O_2$, and Ammonium Tartrate, $(NH_4)_2C_4H_4O_6$.

439. If a solid Sulphate is fused on charcoal with Sodium Carbonate, Na_2CO_3, a residue containing Sodium Sulphid, Na_2S, is produced. If a portion of the fused residue is placed on a bright silver coin and moistened with water, a black stain of Silver Sulphid, Ag_2S, is produced.

SULPHUROUS ACID AND SULPHITES

Formula, H_2SO_3. Anion, SO_3^{--}, and HSO_3^{-}.

440. Altho Sulphurous Acid does not exist in the free state, we assume its presence in solution; because of its property of forming salts with bases, its property of evolving Hydrogen gas with some metals, and its property of conducting the electric current.

Sulphites are more or less insoluble in water, excepting those of the alkali metals, which give colorless solutions.

A solution of Sodium Sulphite, Na_2SO_3, may be used for the following tests:

TESTS

441. Barium Chlorid, $BaCl_2$, produces a white precipitate of Barium Sulphite, $BaSO_3$, which is soluble in acids.

442. Diluted Hydrochloric Acid, HCl, decomposes Sulphites with the evolution of Sulphur Dioxid, SO_2, recognized by its odor (that of burning Sulphur), and its bleaching action on organic coloring matter.

443. Silver Nitrate, $AgNO_3$, produces a white precipitate of Silver Sulphite, $AgSO_3$, soluble in Nitric Acid, HNO_3 and Ammonium Hydroxid. Boiling decomposes the precipitate into metallic Silver, Silver Sulphate, Ag_2SO_4, and Sulphur Dioxid, SO_2.

444. Hydrogen Sulphid, H_2S, decomposes Sulphurous Acid with the separation of Sulphur and the formation of Pentathionic Acid, $H_2S_5O_6$ [ion, $(S_5O_6)^{--}$].

THIOSULPHURIC ACID AND THIOSULPHATES

Formula, $H_2S_2O_3$. Anion, $S_2O_3^{--}$.

445. Thiosulphuric Acid is not known in the free state, but exists in combination with bases as salts known as Thiosulphates (also called Hyposulphites).

The alkali thiosulphates are readily soluble in water, giving colorless solutions; the remainder difficultly soluble.

A solution of Sodium Thiosulphate, $Na_2S_2O_3$, may be used for the following tests:

TESTS

446. Barium Chlorid, $BaCl_2$, produces a white precipitate of Barium Thiosulphate, BaS_2O_3, soluble in a large excess of water. Soluble also in Hydrochloric Acid, HCl, with evolution of Sulphur Dioxid, SO_2, and separation of Sulphur.

447. Ferric Chlorid, $FeCl_3$, added to a solution of an alkali thiosulphate, produces a reddish-violet color, due to the formation of Ferric Thiosulphate, $Fe_2(S_2O_3)_3$. Upon standing, the color finally disappears with formation of colorless Ferrous Chlorid, $FeCl_2$, and alkali Tetrathionate (as $Na_2S_4O_6$). (Distinction from Sulphites.)

448. Diluted Hydrochloric and Sulphuric Acids, HCl and H_2SO_4, produce decomposition with evolution of Sulphur Dioxid, SO_2, recognized by its odor, and the separation of Sulphur.

449. Silver Nitrate, $AgNO_3$, produces a white precipitate of Silver Thiosulphate, $Ag_2S_2O_3$. The precipitate becomes yellow, brown and finally black, due to the formation of Silver Sulphid, Ag_2S.

ORTHOPHOSPHORIC ACID AND ORTHOPHOSPHATES

Formula, H_3PO_4. Anion, PO_4^{---}, HPO_4^{--}, and $H_2PO_4^{-}$.

450. Anhydrous Orthophosphoric Acid occurs in the form of six-sided rhombic prisms. Melting point, 386°C. Easily deliquesces to a thick syrupy liquid. At 260°C. it is converted to Pyrophosphoric Acid, and at 300°C. to Metaphosphoric Acid.

Orthophosphates of the alkalies and alkaline earths (neutral) are soluble in water, giving colorless solutions, the others are soluble in acids.

A solution of Di-sodium Hydrogen Phosphate, Na_2HPO_4, may be used for the following tests:

TESTS

451. Barium Chlorid, $BaCl_2$, produces, in neutral solutions, a white precipitate of Barium Hydrogen Phosphate, $BaHPO_4$, (Barium Phosphate, $Ba_3(PO_4)_2$, in presence of Ammonia), soluble in Hydrochloric, Nitric, and Acetic Acids, HCl, HNO_3, and $HC_2H_3O_2$.

452. Silver Nitrate, $AgNO_3$, produces a yellow precipitate of Silver Phosphate, Ag_3PO_4, soluble in Nitric Acid, HNO_3, and Ammonium Hydroxid, NH_4OH.

453. Magnesia Mixture produces a white crystalline precipitate of Magnesium Ammonium Phosphate, $MgNH_4PO_4$. In dilute solutions the precipitate forms more rapidly if the sides of the vessel are rubbed with a glass rod.

454. Carefully warmed on a *water-bath* with Ammonium Molybdate, $(NH_4)_2MoO_4$, in excess, produces a yellow precipitate of Ammonium Phosphomolybdate, $(NH_4)_3PO_4(MoO_3)_{12}$, in a solution of a Phosphate acidified with Nitric Acid, HNO_3. The precipitate is soluble in Ammonium Hydroxid, NH_4OH, in excess of a Phosphate solution or Orthophosphoric Acid, H_3PO_4. Insoluble in diluted Nitric Acid, HNO_3.

PYROPHOSPHORIC ACID AND PYROPHOSPHATES

Formula, $H_4P_2O_7$. Anion, $P_2O_7^{----}$.

455. PYROPHOSPHORIC ACID occurs in the form of opaque, white crystalline masses. Easily soluble in water.

Pyrophosphates of the alkalis are soluble in water. The others are insoluble or difficultly soluble in water, but soluble in acids.

Use a solution of Sodium Pyrophosphate, $Na_4P_2O_7$.

TESTS

456. Barium Chlorid, $BaCl_2$, produces a white precipitate of Barium Pyrophosphate, $Ba_2P_2O_7$, soluble in acids.

457. Silver Nitrate, $AgNO_3$, produces a white precipitate of Silver Pyrophosphate, $Ag_4P_2O_7$, soluble in Ammonium Hydroxid, NH_4OH, and in Nitric Acid, HNO_3.

458. Solutions of Pyrophosphoric Acid do not coagulate Albumin.

459. On boiling a solution of a Pyrophosphate with Nitric Acid, HNO_3, it is converted to an Orthophosphate.

460. Pyrophosphates are not precipitated by Ammonium Molybdate, $(NH_4)_2MoO_4$, in the cold.

METAPHOSPHORIC ACID AND METAPHOSPHATES

Formula, HPO_3. Anion, PO_3^-.

461. METAPHOSPHORIC ACID occurs in the form of a glassy, hygroscopic mass. The Alkali and Magnesium salts are soluble in water.

Use a solution of Sodium Metaphosphate, $NaPO_3$.

TESTS

462. Barium Chlorid, $BaCl_2$, produces a white precipitate of Barium Metaphosphate, $Ba(PO_3)_2$.

463. Silver Nitrate, $AgNO_3$, produces a white precipitate of Silver Metaphosphate, $AgPO_3$, soluble in Nitric Acid and in Ammonium Hydroxid.

464. Solutions of Metaphosphoric Acid coagulate Albumin solutions. Alkali salts do not.

465. On boiling, Metaphosphoric Acid is converted to Orthophosphoric Acid.

466. Metaphosphates are not precipitated by Ammonium Molybdate, $(NH_4)_2MoO_4$, in the cold.

(ORTHO) BORIC ACID AND BORATES

Formula, H_3BO_3. Anion, BO_3^{---}, (BO_2^-, $B_4O_7^{--}$).

467. (ORTHO) BORIC ACID occurs as transparent, colorless scales of pearly lustre, or in the form of six-sided, triclinic plates. Soluble in 18 parts of water. At 100°C. Orthoboric Acid loses one molecule of water and is converted to METABORIC ACID, HBO_2 (Anion, BO_2^-). When kept at 160°C. for some time the PYROBORIC ACID, $H_2B_4O_7$, (Anion, $B_4O_7^{--}$), is produced. Alkali borates form colorless solutions.

A solution of Sodium Tetraborate (Borax), $Na_2B_4O_7$, may be used for the following tests:

TESTS

468. Barium Chlorid, $BaCl_2$, produces a white precipitate of Barium Metaborate, $Ba(BO_2)_2$, in concentrated solutions. The precipitate is soluble in excess of Barium Chlorid, and in Ammonium Chlorid, NH_4Cl.

469. Borates, moistened with concentrated Sulphuric Acid, H_2SO_4, liberate Boric Acid, H_3BO_3. If Methyl Alcohol, CH_3OH, is added and ignited, a greenish flame is produced. The greenish color imparted to the flame is due to the formation of a volatile ester of Boric Acid, $B(OCH_3)_3$.

470. Tumeric Paper, moistened with a solution of a Borate made slightly acid with Hydrochloric Acid, HCl, and dried, becomes reddish-brown.

471. Silver Nitrate, $AgNO_3$, added to a concentrated solution of a neutral Borate, produces a white precipitate of Silver Metaborate, $AgBO_2$. On warming a brown precipitate of Silver Oxid is obtained. The precipitate is soluble in Nitric Acid, HNO_3, and in Ammonium Hydroxid.

HYDROFLUORIC ACID AND FLUORIDS

Formula, HF. Anion, F^-

472. Pure, anhydrous HYDROFLUORIC ACID is a colorless liquid which boils at 19.4°C. It has the property of etching glass. *The acid should be handled carefully.*

Fluorids of the alkali metals, of Silver, Aluminium, Mercury and Tin, are readily soluble in water, yielding colorless solutions. Those of the alkaline earths, and of Copper, Lead, and Zinc are practically insoluble.

A solution of Potassium Fluorid, KF, or of Sodium, NaF, may be used for the following tests:

TESTS

473. Barium Chlorid, $BaCl_2$, produces a white, bulky precipitate of Barium Fluorid, BaF_2, soluble in Hydrochloric and Nitric Acids, HCl and HNO_3.

474. Calcium Chlorid, $CaCl_2$, produces a gelatinous precipitate of Calcium Fluorid, CaF_2, slightly soluble in cold Hydrochloric Acid, HCl.

475. Mix the dry powdered substance with concentrated Sulphuric Acid, H_2SO_4, in a dish, and cover the dish with a watch-glass, the convex side of which is coated with wax in which some design has been scratched. Fill the watch-glass with water to prevent the melting of the wax when heat is applied. Heat the dish gently for a few minutes. Allow the dish to stand 20 or 30 minutes. Then remove the wax from the watch-glass and the design will appear etched in the glass. The Hydroflouric Acid, formed by the reaction between the alkali fluorid and Sulphuric Acid, reacts with the Silicic Oxid, SiO_2, of the glass, forming volatile Silicon Fluorid, SiF_4.

SILICIC ACID AND SILICATES

Formula, H_2SiO_3. Anion, SiO_3^{--}, (SiO_4^{----}, $Si_2O_5^{--}$, etc.).

476. Pure Silicic Acid is not met with in the free state, but its anhydrid, "Silica" or Silicon Dioxid, SiO_2, is found most abundantly in quartz.

Silicates of the alkali metals are soluble in water. All the other silicates are insoluble in water.

A solution of Sodium Silicate, Na_2SiO_3, may be used for the following tests:

TESTS

477. Barium Chlorid, $BaCl_2$, produces a gelatinous precipitate of Barium Silicate, $BaSiO_3$.

478. Hydrochloric Acid, HCl, produces a gelatinous precipitate, in concentrated solution, of Ortho-silicic Acid, H_4SiO_4. Upon evaporating the mixture to dryness on a water-bath, "Silica" is left as a fine white, amorphous powder.

479. Ammonium Chlorid, NH_4Cl, also precipitates Silicic Acid from concentrated solutions of alkali silicates.

480. If a Silicate is fused in a bead of Sodium Metaphosphate, $NaPO_3$, an insoluble skeleton of Silica is obtained.

CARBONIC ACID AND CARBONATES

Formula, H_2CO_3. Anion, CO_3^{--} and HCO_3^-.

481. CARBONIC ACID is not known in the free state, but is supposed to exist in aqueous solution charged with Carbon Dioxid, CO_2. Its anhydrid, CO_2, is a colorless, odorless gas, with a weak acid taste, and 1.529 times heavier than air.

Carbonates and Bicarbonates of the alkali metals are soluble in water, yielding colorless solutions. Other carbonates are insoluble in water. The *Bicarbonates* of certain metals, like Magnesium, Calcium, Strontium, etc., are soluble in water.

A solution of Sodium Carbonate, Na_2CO_3, may be used for the following tests:

TESTS

482. Barium Chlorid, $BaCl_2$, produces a white precipitate of Barium Carbonate, $BaCO_3$, soluble with effervescence in diluted acids.

483. Diluted Acids (except Hydrocyanic, HCN, and Sulphydric, H_2S) produce an effervescence, due to evolution of Carbon Dioxid gas. If the liberated gas is passed into a tube containing clear Calcium Hydroxid, $Ca(OH)_2$, solution (Lime Water), a turbidity is produced due to the formation of insoluble Calcium Carbonate, $CaCO_3$.

484. Silver Nitrate, $AgNO_3$, produces a white precipitate of Silver Carbonate, Ag_2CO_3, soluble in Nitric Acid and Ammonium Hydroxid.

CHROMIC ACID AND CHROMATES

Formula, H_2CrO_4. Anion, CrO_4^{--} and $Cr_2O_7^{--}$.

485. CHROMIC ACID cannot be isolated. The anhydrid, CrO_3, is red, crystalline, very soluble, and a powerful oxidizing agent.

Chromates of Calcium, Strontium, Magnesium and the alkali metals are soluble in water. Most of the others are insoluble. Solutions of the chromates are yellow. The Dichromates (Compounds of the Anion $Cr_2O_7^{--}$) are soluble, yielding a deep reddish-yellow solution.

A solution of Potassium Chromate, K_2CrO_4, may be used for the following tests:

TESTS

486. Barium Chlorid, $BaCl_2$ produces a yellow precipitate of Barium Chromate, $BaCrO_4$, soluble in Hydrochloric and Nitric Acids, HCl and HNO_3.

487. Hydrogen Sulphid, H_2S, in the presence of Hydrochloric Acid, HCl, reduces solutions of Chromates forming soluble Chromium Chlorid, $CrCl_3$ (Chromic ion), and precipitating Sulphur. The color changes from yellow to green.

488. Lead Acetate, $Pb(C_2H_3O_2)_2$, produces a yellow, crystalline precipitate of Lead Chromate, $PbCrO_4$, insoluble in water and Acetic Acid, $HC_2H_3O_2$. Soluble in Nitric Acid, HNO_3, and Sodium Hydroxid, NaOH.

489. Silver Nitrate, $AgNO_3$, produces a purplish-red precipitate of Silver Chromate, Ag_2CrO_4, soluble in Nitric Acid, HNO_3, and Ammonium Hydroxid, NH_4OH.

490. Hydrogen Dioxid, H_2O_2, added to a dilute solution of a Chromate acidified with Hydrochloric Acid, HCl, produces a blue coloration, due to formation of Perchromic Acids. Results are only secured with dilute solutions. If the mixture is shaken with Ether, $(C_2H_5)_2O$, the blue compound is extracted from the water and the ethereal layer becomes blue in color.

ARSENIOUS ACID AND ARSENITES

Formula, H_3AsO_3. Anion, AsO_3^{---}, and $HAsO_3^{--}$.

491. ARSENIOUS ACID is not known in the free state, for upon liberation from its salts, it breaks up into its anhydrid and water:—$2H_3AsO_3 = As_2O_3 + 3H_2O$.

An alkaline solution of Sodium Metarsenite, $NaAsO_2$, may be used for the tests.

TESTS

492. Employ the Tests described under Arsenious Compounds on Pages 79–81.

ARSENIC ACID (Ortho) AND ARSENATES

Formula, H_3AsO_4. Anion, AsO_4^{---}, $HAsO_4^{--}$.

493. Free ARSENIC ACID cannot be isolated, its anhydrid, As_2O_5, is obtained instead. Heated to 180°C. brings about a conversion to PYROARSENATE $As_2O_7^{----}$, and at 200°C. to METARSENATE AsO_3^{-}. When heated to redness, a glassy mass of Arsenic Pentoxid, As_2O_5, is formed.

A solution of Sodium Arsenate, Na_2HAsO_4, may be used for the tests:

TESTS

494. Employ the Tests described under Arsenic Compounds on Pages 81–82.

OXALIC ACID AND OXALATES

Formula, $H_2C_2O_4$. Anion, $C_2O_4^{--}$ and $HC_2O_4^{-}$.

495. OXALIC ACID occurs in colorless, four-sided, prismatic crystals, resembling closely those of Magnesium Sulphate. Soluble in water and Alcohol.

Oxalates of the alkali metals and of Magnesium are soluble in water, forming colorless solutions. Most of the others are insoluble.

A solution of Ammonium Oxalate $(NH_4)_2C_2O_4$, may be used for the following tests:

TESTS

496. Barium Chlorid, $BaCl_2$, produces a white precipitate of Barium Oxalate, BaC_2O_4, soluble in Nitric and Hydrochloric Acids, HNO_3 and HCl.

497. Calcium Chlorid, $CaCl_2$, produces a white precipitate of Calcium Oxalate, CaC_2O_4, soluble in Hydrochloric and Nitric Acids, HCl and HNO_3. Insoluble in Acetic Acid, $HC_2H_3O_2$.

498. Calcium Sulphate, $CaSO_4$, gives the same precipitate as the preceding.

499. Silver Nitrate, $AgNO_3$, produces a white precipitate of Silver Oxalate, $Ag_2C_2O_4$, soluble in Nitric Acid, HNO_3 and Ammonium Hydroxid, NH_4OH.

500. When Oxalates or Oxalic Acid are heated with concentrated Sulphuric Acid, H_2SO_4, they are decomposed with the evolution of Carbon Monoxid and Carbon Dioxid, CO and CO_2. If the evolved gases are passed into a tube containing a clear solution of Calcium Hydroxid, $Ca(OH)_2$, (Lime Water), the precipitated Calcium Carbonate, $CaCO_3$, indicates the presence of Carbon Dioxid.

501. Upon ignition, Oxalates of the Alkalies and Alkaline Earths are decomposed into Carbon Dioxid, CO_2, and Carbonates or Oxids of the metals which were in combination as Oxalates.

TARTARIC ACID AND TARTRATES

Formula, $H_2C_4H_4O_6$. Anion, $C_4H_4O_6^{--}$ and $HC_4H_4O_6^{-}$.

502. Tartaric Acid occurs in the form of colorless, translucent, odorless, monoclinic prisms, or in the form of a white powder. It has a purely acid taste. Very soluble in water. Melts at about 170°C.

Neutral Tartrates of the alkali metals are soluble in water, forming colorless solutions. Most of the others are soluble with difficulty.

A solution of Potassium Sodium Tartrate, $KNaC_4H_4O_6$, may be used for the following tests:

TESTS

503. Barium Chlorid, $BaCl_2$, produces a white precipitate of Barium Tartrate, $BaC_4H_4O_6$, soluble in Hydrochloric and Nitric Acids, HCl and HNO_3, and Ammonium salts.

504. Calcium Chlorid, $CaCl_2$, produces a white, crystalline precipitate of Calcium Tartrate, $CaC_4H_4O_6$, soluble in Hydrochloric, Nitric and Acetic Acids, HCl, HNO_3, $HC_2H_3O_2$. Also in Sodium and Potassium Hydroxids, NaOH and KOH, in the *cold*, but is reprecipitated upon boiling.

505. Silver Nitrate, $AgNO_3$, produces, in neutral solutions, a white precipitate of Silver Tartrate, $Ag_2C_4H_4O_6$., On adding Ammonium Hydroxid, NH_4OH, to the fluid containing the precipitate until the latter is almost dissolved and then heating at about 70°C., a mirror of metallic Silver forms on the inside of the tube. The free acid is not precipitated.

506. Potassium Acetate, $KC_2H_3O_2$, in the presence of free Acetic Acid, $HC_2H_3O_2$, produces, in concentrated solutions, a white precipitate of Potassium Hydrogen Tartrate, $KHC_4H_4O_6$.

507. Tartrates, on being ignited alone or with Sulphuric Acid, H_2SO_4, are decomposed with the production of an odor resembling that of burnt sugar, the mixture being carbonized and SO_2 liberated.

CITRIC ACID AND CITRATES

Formula, $H_3C_6H_5O_7$. Anion, $C_6H_5O_7^{---}$.

508. Citric Acid occurs in the form of colorless, odorless, translucent, right-rhombic prisms having an agreeable acid taste. Very soluble in water.

Alkali citrates are soluble in water and form soluble complex salts with the insoluble citrates of the heavy metals. The anion is colorless.

A solution of Sodium Citrate, $Na_3C_6H_5O_7$, may be used for the following tests:

TESTS

509. Calcium Chlorid, $CaCl_2$, in excess produces, in the presence of Potassium or Sodium Hydroxid or Alcohol, a white precipitate of Calcium Citrate, $Ca_3(C_6H_5O_7)_2$, soluble in Ammonium Chlorid, NH_4Cl. Free Citric Acid is not precipitated by Calcium Chlorid.

510. Lime Water (Solution of Calcium Hydroxid) $Ca(OH)_2$, in excess, produces no precipitate in a cold solution. On boiling, Calcium Citrate, $Ca_3(C_6H_5O_7)_2$, separates out, and dissolves again on cooling. (Tartrates are precipitated in the cold by Calcium Hydroxid.)

511. Barium Acetate, $Ba(C_2H_3O_2)_2$, produces an amorphous precipitate of Barium Citrate, $Ba_3(C_6H_5O_7)_2$, in solutions of alkali citrates. On boiling with an excess the reagent, the amorphous precipitate passes into a crystalline salt having the formula $2Ba_3(C_6H_5O_7)_2.7H_2O$. Soluble in Acids and Ammonium salts.

512. When gradually heated to 75°C. the Acid loses its water of crystallization. If subjected to stronger heat it fuses and then carbonizes, emitting irritant fumes which have not the odor of burnt sugar. (Distinction from Tartrates.)

CHAPTER XVII

Group B

513. Acids or Anions precipitated from dilute Nitric Acid solutions by Silver Nitrate.

In this Group are found, Chlorids, Bromids, Iodids, Cyanids, Ferrocyanids, Ferricyanids, Thiocyanates, Sulphids, Nitrites, Hypochlorites, and Hypophosphites.

HYDROCHLORIC ACID AND CHLORIDS

Formula, HCl. Anion, Cl^-.

514. Hydrochloric Acid is a colorless gas, having a sharp, suffocating odor and acid taste. S./G., 1.269. Very soluble in water.

All chlorids are soluble in water with the exceptions of Silver, Mercurous, Cuprous, Platinous, Aurous, and Lead Chlorids, the last, however, is soluble in hot water.

A solution of Sodium Chlorid, $NaCl$, may be used for the following tests:

TESTS

515. Silver Nitrate, $AgNO_3$, produces a white precipitate of Silver Chlorid, $AgCl$, which becomes violet and finally black upon exposure to sunlight. The precipitate is soluble in Ammonium Hydroxid, NH_4OH, Potassium Cyanid, KCN, and Sodium Thiosulphate, $Na_2S_2O_3$. Insoluble in HNO_3.

516. Lead Acetate, $Pb(C_2H_3O_2)_2$, produces a white precipitate of Lead Chlorid, $PbCl_2$, soluble in large excess of cold water, and easily soluble in hot water. Insoluble in strong Hydrochloric Acid.

517. Solid Chlorids, or strong solutions of Chlorids, when strongly heated with concentrated Sulphuric Acid, H_2SO_4, yield free Hydrochloric Acid, HCl, which may be detected by its odor and the heavy white fumes obtained by holding a rod, moistened with Ammonium Hydroxid, over the vessel in which the reaction is carried out.

518. Solid Chlorids, or strong solutions of Chlorids, heated with Manganese Dioxid, MnO_2, and concentrated Sulphuric Acid, H_2SO_4, evolve free Chlorin upon application of heat. This may be detected by its odor, bleaching action on moist organic coloring matter, and its action on moist paper impregnated with Potassium Iodid and Starch. With the last, Iodin is liberated and forms a blue compound with the Starch.

519. A dry Chlorid, mixed with one-half its weight of Potassium Dichromate $K_2Cr_2O_7$, and some Sulphuric Acid, H_2SO_4, and distilled, yields a deep, brownish-red gas, Chlorochromic Anhydrid, CrO_2Cl_2, which condenses into a liquid of the same color. If Ammonium Hydroxid, NH_4OH, is added to the distillate, a yellow liquid is produced, due to the formation of Ammonium Chromate, $(NH_4)_2CrO_4$, which in turn may be precipitated by Lead Acetate solution.

HYDROBROMIC ACID AND BROMIDS

Formula, HBr. Anion, Br^-.

520. Hydrobromic Acid is a colorless, heavy gas with a sharp, irritating odor and acid taste. S./G., 2.8. Very soluble in water.

Most Bromids are soluble in water with the exception of Silver, Mercurous, Platinous and Aurous. Lead and Cuprous are very slightly soluble. Solutions are colorless.

A solution of Potassium Bromid, KBr, may be used for the following tests:

TESTS

521. Silver Nitrate, $AgNO_3$, produces a curdy, yellowish precipitate of Silver Bromid, AgBr, insoluble in diluted Nitric Acid, HNO_3, soluble in Ammonium Hydroxid, NH_4OH, Potassium Cyanid, KCN, and Sodium Thiosulphate, $Na_2S_2O_3$.

522. Lead Acetate, $Pb(C_2H_3O_2)_2$, produces a white crystalline precipitate of Lead Bromid, $PbBr_2$, sparingly soluble in cold water, but more soluble in hot.

523. Solid Bromids, heated with concentrated Sulphuric Acid, H_2SO_4, and Manganese Dioxid, MnO_2, evolve free Bromin, which is recognized by its color and odor.

524. When a solution of a Bromid is treated with Chlorin gas or Chlorin Water, the Bromid is decomposed with liberation of free Bromin, which colors the fluid yellow or reddish-yellow. *An excess of Chlorin must be avoided*, as this would convert the molecular Bromin to colorless Bromate ion, BrO_3^-. The free Bromin may be dissolved out by shaking with Carbon Disulphid, CS_2, or Chloroform, $CHCl_3$, which collects at the bottom of the tube as a reddish-yellow liquid.

525. A solid Bromid, mixed with about one-half its weight of Potassium Dichromate, $K_2Cr_2O_7$, and some concentrated Sulphuric Acid, H_2SO_4, yields, when the mixture is heated in a distillation apparatus, free Bromin, which condenses in the receiver. If Ammonium Hydroxid, NH_4OH, is added, a colorless solution results because of the formation of Ammonium Bromid, NH_4Br, and Ammonium Bromate, NH_4BrO_3. (See Chlorids.)

HYDRIODIC ACID AND IODIDS

Formula, HI. Anion, I^-.

526. Hydriodic Acid is a colorless, heavy gas with a sharp, irritating odor and acid taste. S./G., 4.42. Very soluble in water.

Nearly all iodids are very soluble in water; Silver, Mercurous, Lead, Mercuric, and Cuprous Iodids are exceptions. Solutions are colorless.

A solution of Potassium Iodid, KI, may be used for the following tests:

TESTS

527. Silver Nitrate, $AgNO_3$, produces a yellowish, amorphous precipitate, of Silver Iodid, AgI, insoluble in Nitric Acid, HNO_3, very slightly soluble in Ammonium Hydroxid, NH_4OH. Soluble in Potassium Cyanid, KCN, and Sodium Thiosulphate, $Na_2S_2O_3$.

528. Lead Acetate, $Pb(C_2H_3O_2)_2$, produces a yellow, crystalline precipitate of Lead Iodid, PbI_2, slightly soluble in hot water, from which, upon cooling, it separates out in yellow, six-sided plates.

529. Solid Iodids, heated with concentrated Sulphuric Acid, H_2SO_4, and Manganese Dioxid, MnO_2, evolve free Iodin in the vaporous condition. This is recognized by its deep violet color. If the vapors are allowed to act upon starch paper a deep blue color is produced.

530. When a solution of an Iodid is treated with Chlorin Gas or Chlorin Water, the Iodid is decomposed with liberation of free Iodin, which colors the fluid reddish-brown. *An excess of Chlorin must be avoided*, as this would convert the molecular Iodin (thru oxidation by the chlorin) in the presence of water, to the colorless Iodate ion, IO_3^-. The free Iodin may be dissolved out by shaking with Carbon Disulphid, CS_2, or Chloroform, $CHCl_3$, which collects at the bottom of the tube as a violet-colored liquid.

531. Copper Sulphate, $CuSO_4$, added to a neutral solution produces a dirty white precipitate of Cuprous Iodid, CuI. Chlorids and Bromids are not precipitated by this reagent.

HYDROCYANIC ACID AND CYANIDS*

Formula, HCN. Anion, CN^-.

532. Hydrocyanic Acid, or "Prussic Acid," is a colorless liquid, boiling at 26.5°C., and solidifying at 15°C. It is miscible with water and is a deadly poison.

Cyanids of the alkalis and alkaline earths and of Mercury (*ic*) are soluble in water, forming colorless solutions.

A solution of Potassium Cyanid, KCN, may be used for the following tests:

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* Extreme care should be observed in working with this acid and its salts because they are deadly poisons.

TESTS

533. Silver Nitrate, $AgNO_3$, produces a white, curdy precipitate of Silver Cyanid, AgCN, soluble in Ammonium Hydroxid, NH_4OH, but insoluble in *dilute* Nitric Acid, The precipitate appears only after adding an excess of Silver Nitrate, since Silver Cyanid is soluble in Potassium Cyanid, KCN, ($Ag(CN)_2^-$). On igniting, Silver Cyanid decomposes yielding metallic Silver and Cyanogen, $(CN)_2$.*

534. Lead Acetate, $Pb(C_2H_3O_2)_2$, produces a white precipitate of Lead Cyanid, $Pb(CN)_2$, soluble in Nitric Acid, HNO_3.

535. If Sodium Hydroxid, NaOH, Ferrous Sulphate, $FeSO_4$, and Ferric Chlorid, $FeCl_3$, are added to a Cyanid solution, the mixture warmed, and then made acid with Hydrochloric Acid, HCl, a blue precipitate of Ferric Ferrocyanid, $Fe_4(Fe(CN)_6)_3$, is formed.

536. The addition of Ammonium Hydroxid, NH_4OH, until alkaline in reaction, followed by the addition of two or three drops of Ammonium Poly-sulphid, and warmed, yields a blood-red color upon the further addition of Hydrochloric Acid, HCl, until faintly acid, and Ferric Chlorid, $FeCl_3$. The red color is due to the formation of soluble Ferric Thiocyanate, $Fe(CNS)_3$.

THIOCYANIC ACID AND THIOCYANATES

Formula, HCNS. Anion, CNS^-.

537. THIOCYANIC ACID is a colorless, oily liquid, boiling at 85°C., and solidifying at $-12.5°C$. It has a penetrating odor, and is miscible with water and Alcohol.

Thiocyanates of the alkalis, alkaline earths, and heavy metals, with the exceptions of Silver, Copper, Gold and Mercury, are soluble in water.

A solution of Potassium Thiocyanate, KCNS, may be used for the following tests:

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* A very poisonous gas.

TESTS

538. Silver Nitrate, $AgNO_3$, produces a white, curdy precipitate of Silver Thiocyanate, AgCNS, insoluble in dilute Nitric Acid, HNO_3, but soluble in Ammonium Hydroxid, NH_4OH.

539. Lead Acetate, $Pb(C_2H_3O_2)_2$, produces a white precipitate of Lead Thiocyanate, $Pb(CNS)_2$.

540. Ferric Chlorid, $FeCl_3$, produces a deep-red color, due to the formation of Ferric Thiocyanate, $Fe(CNS)_3$. In dilute solutions the color is pale red.

541. Copper Sulphate, $CuSO_4$, produces a dark precipitate of Cupric Thiocyanate, $Cu(CNS)_2$, which gradually changes to the stable Cuprous Compound, CuCNS.

HYDROFERROCYANIC ACID AND FERROCYANIDS

Formula, $H_4Fe(CN)_6$. Anion, $Fe(CN)_6^{----}$.

542. HYDROFERROCYANIC or FERROCYANIC ACID is colorless, crystalline, and readily soluble in water. Its solution has a strong acid reaction.

The ferrocyanids of the alkalis and alkaline earths are soluble in water, giving pale yellow solutions. Most of the remaining are insoluble.

A solution of Potassium Ferrocyanid, $K_4Fe(CN)_6$ may be used for the following tests:

TESTS

543. Silver Nitrate, $AgNO_3$, produces a white precipitate of Silver Ferrocyanid, $Ag_4Fe(CN)_6$, soluble in Potassium Cyanid, KCN. Insoluble in dilute Nitric Acid, HNO_3, and Ammonium Hydroxid, NH_4OH.

544. Lead Acetate, $Pb(C_2H_3O_2)_2$. produces a white precipitate of Lead Ferrocyanid, $Pb_2Fe(CN)_6$, insoluble in diluted Nitric Acid, HNO_3.

545. Ferrous Sulphate, $FeSO_4$, in excess, produces a white precipitate of Ferrous Ferrocyanid, $Fe_2Fe(CN)_6$, which readily changes to blue Ferric Ferrocyanid, $Fe_4(Fe(CN)_6)_3$, thru oxidation by the air.

546. Ferric Chlorid, $FeCl_3$, produces a dark blue precipitate of Ferric Ferrocyanid, $Fe_4(Fe(CN)_6)_3$, Prussian Blue, insoluble in diluted acids. Decomposed by excess of alkali hydroxids with separation of Ferric Hydroxid, $Fe(OH)_3$.

547. Copper Sulphate, $CuSO_4$, produces a reddish-brown precipitate of Copper Ferrocyanid, $Cu_2Fe(CN)_6$, insoluble in diluted acids. Decomposed by alkali hydroxids.

HYDROFERRICYANIC ACID AND FERRICYANIDS

Formula, $H_3Fe(CN)_6$. Anion, $Fe(CN)_6^{---}$.

548. Hydroferricyanic or Ferricyanic Acid occurs as soluble brown needles. The ferricyanids of the alkalis and alkaline earths are soluble in water. Those of the heavy metals are insoluble, except the Ferric salt. In solution, these salts are rapidly reduced and Ferrocyanid formed. *In alkaline solution Ferrocyanid only exists.*

A solution of Potassium Ferricyanid, $K_3Fe(CN)_6$, may be used for the following tests:

TESTS

549. Silver Nitrate, $AgNO_3$, produces a brownish precipitate of Silver Ferricyanid, $Ag_3Fe(CN)_6$, insoluble in Nitric Acid, but soluble in Potassium Cyanid, KCN, and Ammonium Hydroxid, NH_4OH.

550. Lead Acetate, $Pb(C_2H_3O_2)_2$, gives no precipitate.

551. Ferrous Sulphate, $FeSO_4$, produces a blue precipitate of Ferrous Ferricyanid, $Fe_3(Fe(CN)_6)_2$, and Potassium-Ferric Ferrocyanid, $KFe(FeCN)_6$, (Turnbull's Blue), if acid or neutral, insoluble in diluted acids. Decomposed by alkali hydroxids.

552. Ferric Chlorid, $FeCl_3$, does not produce a precipitate, but colors the solution brown.

553. Copper Sulphate, $CuSO_4$, produces a greenish-yellow precipitate of Copper Ferricyanid, $Cu_3(Fe(CN)_6)_2$, insoluble in Hydrochloric Acid, HCl.

SULPHYDRIC ACID AND SULPHIDES

Formula, H_2S. Anion, S^{--}, (HS^-).

554. Sulphydric Acid is a colorless gas with a disagreeable odor and sweetish taste. S./G., 1.18. It is soluble in water. Condenses to a liquid under pressure of 17 atmospheres, which boils at −68.8°C., and solidifies at −85°C.

The sulphids, with the exception of those of the alkalis and alkaline earths, are insoluble in water. Solutions are colorless and unstable.

A solution of Sodium Sulphid, Na_2S, or Ammonium Sulphid, $(NH_4)_2S$, may be used for the following tests:

TESTS

555. Silver Nitrate, $AgNO_3$, produces a black precipitate of Silver Sulphid, Ag_2S, soluble in hot Nitric Acid, HNO_3, and in Potassium Cyanid, KCN.

556. Lead Acetate, $Pb(C_2H_3O_2)_2$, produces a black precipitate of Lead Sulphid, PbS, soluble in hot Nitric Acid, HNO_3.

557. Sodium Nitroprussid, $Na_2NOFe(CN)_5$, added to a solution of a Sulphid in the presence of an alkali, produces a violet-red color.

558. Most Sulphids are decomposed when warmed with diluted Hydrochloric or Sulphuric Acids, HCl or H_2SO_4, yielding Hydrogen Sulphid gas, H_2S, which may be recognized by its odor, or by its action on paper moistened with Lead Acetate solution, $Pb(C_2H_3O_2)_2$, which the gas turns black, due to formation of Lead Sulphid, PbS.

NITROUS ACID AND NITRITES

Formula, HNO_2. Anion, NO_2^-.

559. Nitrous Acid is not known in the free state. It is formed by adding liquid Nitrogen Trioxid, N_2O_3, to ice water, but, because of its instability, it breaks up into Nitric Acid, HNO_3, and Nitric Oxid, NO. Its salts, the Nitrites, are fairly stable.

All nitrites are soluble in water, except Silver Nitrite and Potassium Cobaltic Nitrite, which are soluble with difficulty.

A solution of Potassium Nitrite, KNO_2, may be used for the following tests:

TESTS

560. Silver Nitrate, $AgNO_3$, produces a white precipitate of Silver Nitrite, $AgNO_2$, soluble with difficulty in water.

561. Treated with Hydrochloric Acid, HCl, or Sulphuric Acid, H_2SO_4, Nitrites evolve brownish-red fumes of Nitrogen Dioxid, NO_2.

562. A Nitrite solution, acidified with diluted Sulphuric Acid, H_2SO_4, produces a blue color when mixed with starch paste containing Potassium Iodid, KI, because of the NO_2 liberated which liberates the Iodin from the Potassium Iodid.

563. Nitrous Acid is oxidized to Nitric Acid, HNO_3, by permanganates. Therefore, on the addition of Potassium Permanganate, $KMnO_4$, to an acidified solution of a Nitrite, the Potassium Permanganate will be reduced upon warming.

HYPOCHLOROUS ACID AND HYPOCHLORITES

Formula, HClO. Anion, ClO^-.

564. Hypochlorous Acid is known only in solution, which is colorless when dilute, and yellowish when more concentrated. This acid and its salts possess strong oxidizing and bleaching properties, thru the liberation of nascent oxygen. All salts are soluble in water.

A solution of Sodium Hypochlorite, NaClO, may be used for the following tests:

TESTS

565. Silver Nitrate, $AgNO_3$, produces soluble Silver Hypochlorite, AgClO, which immediately breaks up into white, insoluble Silver Chlorid, $AgCl$, and soluble Silver Chlorate, $AgClO_3$.

566. Lead Acetate, $Pb(C_2H_3O_2)_2$, produces, at first, a white precipitate of Lead Chlorid, $PbCl_2$, which rapidly changes to yellow and finally brown, due to the formation of PbO_2, Lead Dioxid.

567. Chlorin is liberated from a Hypochlorite by the addition of a diluted acid.

568. Acid solutions of litmus, indigo, and many other organic coloring matters are bleached by the addition of a Hypochlorite solution.

HYPOPHOSPHOROUS ACID AND HYPOPHOSPHITES

Formula, HPH_2O_2. Anion, $PH_2O_2^-$.

569. Hypophosphorous Acid is a colorless, thick, syrupy liquid of strong acid reaction. It is a powerful reducing agent.

All hypophosphites are soluble in water.

A solution of Sodium Hypophosphite, $NaPH_2O_2$, may be used for the following tests:

TESTS

570. Silver Nitrate, $AgNO_3$, produces a white precipitate of Silver Hypophosphite, $AgPH_2O_2$, which rapidly becomes black, due to reduction to metallic Silver.

571. Mercuric Chlorid, $HgCl_2$, produces a white precipitate of Mercurous Chlorid, $HgCl$, which on heating turns gray-black, due to reduction to metallic Mercury.

572. Solid Hypophosphites heated in a dry tube causes decomposition with evolution of Hydrogen Phosphid, PH_3,* which has a characteristic, disagreeable odor, and inflames when heated to 100°C., yielding a white cloud of Phosphoric Oxid, P_2O_5.

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* A very poisonous gas.

CHAPTER XVIII

Group C

573. Acids or Anions not precipitated by BARIUM CHLORID or SILVER NITRATE.

In this Group are found Nitrates, Chlorates and Acetates.

NITRIC ACID AND NITRATES

Formula, HNO_3. Anion, NO_3^-.

574. NITRIC ACID is a colorless, fuming, very corrosive liquid. Solidifies at -47°C. When absolute (99.8%) it boils at 86°C. and has a S./G. of 1.50. The 68% (U. S. P.) acid has a S./G. of 1.403.

All nitrates, with the exception of basic salts, are soluble in water. The anion is colorless.

A solution of Potassium Nitrate, KNO_3, may be used for the following tests:

TESTS

575. Solid Nitrates deflagrate when heated on charcoal.

576. If equal volumes of concentrated Sulphuric Acid, H_2SO_4, and a nitrate solution are mixed in a test-tube, and the mixture cooled, the addition of Ferrous Sulphate, $FeSO_4$, solution poured into the tube so that the liquids do not mix, causes the formation of a brown ring at the junction of the two liquids. This brown ring is due to the oxidation of the ferrous compound, and the subsequent reduction of the Nitric Acid to Nitric Oxid, NO, which combines with the excess of Ferrous Sulphate to form the unstable compound, $4(FeSO_4)NO$. Chlorates, Iodids, Bromids, and Chromates interfere with this reaction.

577. Potassium Iodid, KI, Starch paste, and diluted Sulphuric Acid, H_2SO_4, added to a nitrate solution produce no reaction. (Distinction from Nitrites.)

578. If a few drops of a solution of Brucin in Sulphuric Acid, H_2SO_4 (0.2 Gm. in 100 Cc.), is brought in contact with a drop of a nitrate solution, a deep red color develops at the point of contact of the liquids. The color gradually fades to yellow and finally greenish.

CHLORIC ACID AND CHLORATES

Formula, $HClO_3$. Anion, ClO_3^-.

579. CHLORIC ACID is known only in solution and in combination with certain bases as Chlorates. In solution it may be concentrated to 40% by evaporation over Sulphuric Acid. On further concentration it decomposes. When of the foregoing strength, Chloric Acid is a syrupy, colorless liquid, with a faint chlorous odor. Its chemical properties resemble those of Nitric Acid.

All chlorates are soluble in water.

A solution of Potassium Chlorate, $KClO_3$, may be used for the following tests:

TESTS

580. A dry Chlorate, when warmed with Sulphuric Acid, H_2SO_4, evolves a greenish-yellow explosive gas, Chlorin Tetroxid, Cl_2O_4, having a chlorous odor. This test should be carried out with very small quantities of a Chlorate because of the explosive nature of the gas. The Chlorate is decomposed with the production of Chlorin Tetroxid and Perchloric Acid.

581. On warming a solution of a Chlorate with Hydrochloric Acid, HCl, the liquid becomes greenish-yellow, and greenish-yellow fumes are evolved. The fumes consist of a mixture of Chlorin and Chlorin Dioxid.

582. When heated in a reduction-tube, Chlorates undergo decomposition, and are converted into Chlorids with evolution of Oxygen.

ACETIC ACID AND ACETATES

Formula, $HC_2H_3O_2$. Anion, $C_2H_3O_2^-$.

583. Pure ACETIC ACID is a strongly acid, clear, colorless liquid of pungent odor and purely acid taste. It solidifies in the cold to crystalline plates. Melting Point, 15°C. Boiling Point, 118°C. S./G., 1.055.

All acetates are readily soluble in water, excepting silver, which is difficultly soluble. Solutions containing Aluminium, Chromium and Ferric Acetates are decomposed into sparingly soluble basic Acetates when boiled.

A solution of Sodium Acetate, $NaC_2H_3O_2$, may be used for the following tests:

TESTS

584. Add to the solution of the Acetate, or to a portion of dry material, an equal volume of diluted Sulphuric Acid, H_2SO_4, and about 10 drops of Alcohol, C_2H_5OH. Apply a gentle heat. By this treatment Ethyl Acetate, $C_2H_5C_2H_3O_2$, is formed, and is recognized by its characteristic, agreeable odor. The student should carry out this test a number of times so as to become familiar with the odor of Ethyl Acetate. Overheating causes evolution of SO_2, which covers the odor of the ester. The presence of Nitrites, NO_2^-, masks this test. If Nitrites are present, Sulphuric Acid, H_2SO_4, should be first added and the mixture heated to expel the fumes of Nitrogen Dioxid, NO_2, *then cooled*, and the very small amount of Alcohol added.

585. Ferric Chlorid, $FeCl_3$, added to a solution of a neutral Acetate, produces a deep red fluid, which, *on boiling*, yields a reddish-brown precipitate of Basic Ferric Acetate, $Fe(OH)(C_2H_3O_2)_2$ or $Fe(OH)_2C_2H_3O_2$.

586. Silver Nitrate, $AgNO_3$, added to *concentrated* solutions of Acetates, produces a white, crystalline precipitate of Silver Acetate, $AgC_2H_3O_2$, which dissolves in large excess of water and in Ammonium Hydroxid, NH_4OH.

CHAPTER XIX

Detection of the Acids or Anions

587. The determination of the Metals (Cations) present should always precede the examination for the Acids (Anions) since the presence of certain Metals excludes the presence of certain Acids. For example:—If Barium is found in the solution under examination, it would be useless to test for Sulphuric Acid, since Barium forms an insoluble compound with the Acid mentioned.

588. The physical properties of the material under examination may often suggest what to look for. For example:—Metals or Alloys would not be tested for Acids. The solubility and the color of the substance will also assist in simplifying matters. For example:—A colorless mixture could not contain a Chromate, Dichromate or Manganate. The odor, hardness, specific gravity, etc., are also of much importance.

589. After detecting the Metals present by applying the methods described in the preceding chapters [that is: (1) Adding to the solution, or a solution of the solid under examination, Hydrochloric Acid and filtering; (2) Examining the precipitate, if any, for the members of Group 1; (3) Adding Hydrogen Sulphid to the filtrate and filtering; (4) Examining the second precipitate, if any, for the members of Group 2 and Group 3 as described; (5) Adding Ammonium Hydroxid to the filtrate from Groups 2 and 3, and filtering again; (6) Examining this third precipitate for the members of Group 4; (7) Adding to the filtrate from Group 4 Hydrogen Sulphid, and filtering; (8) Examining this precipitate, if any, for the members of Group 5; (9) Adding to the filtrate from Group 5 Ammonium Carbonate and filtering; (10) Examining this precipitate if any, for the members of Group 6; (11) Examining the filtrate from Group 6 for the members of Group 7]; the student is ready for the detection of the Anions.

590. The following preliminary tests on portions of the *dry* material may be made *before* proceeding with tests on a solution of the substance for the Acids or Anions. If a solution is to be examined, it must be freed from Ammonium salts, and a portion of it may be carefully evaporated to dryness on a water-bath, and portions of the dried residue used for the following tests:

I—Tests on the Dry Substance

591. Heat a portion in a dry tube:

I—CARBONIZATION indicates the presence of ORGANIC ACIDS. (Citrates, Oxalates, Tartrates and sometimes Acetates, ¶594, 619.)

II—WATER VAPOR indicates the presence of Hydroxids of heavy metals $[(OH)_2^{--} \rightarrow H_2O + O]$ or substances containing water of crystallization.

III—LIBERATION OF A GAS INDICATES:—

(*a*)—If Oxygen (inflames a spark)—CHLORATES, IODATES, BROMATES, PEROXIDS, NITRATES.* (¶579, 574.)

(*b*)—If Carbon Dioxid (colorless, odorless, and produces a turbidity in lime water)—CARBONATES, BICARBONATES, OXALATES, TARTRATES, CITRATES. (¶481, 495, 502, 508.)

(*c*)—If Sulphur Dioxid (odor of burning Sulphur)—SULPHATES, *with reducing agents;* SULPHITES; SULPHIDS, *with air;* THIOSULPHATES. (¶436, 440, 445, 554.)

(*d*)—If Oxids of Nitrogen (brownish-red and odor)—NITRITES, NITRATES. (¶559, 574.)

(*e*)—If Chlorin, Bromin, and Iodin (yellowish-green, brownish-red and violet, and odors)—CHLORIDS, BROMIDS, IODIDS. (¶514, 520, 526, 607.)

(*f*)—If Cyanogen† (odor of bitter almonds and inflammable)—CYANIDS. (¶532.)

(*g*)—If Hydrogen Sulphid (colorless, but odor and blackens Lead Acetate paper)—SULPHIDS. (¶554.)

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* See footnote, page 166.

† A very poisonous gas.

(*h*)—If Ammonia (odor and turns red litmus blue) —AMMONIUM SALTS, CYANIDS. (¶532.)

(*i*)—If Hydrogen Phosphid* (takes fire in tube and burns from bottom of tube up, odor of garlic)—HYPOPHOSPHITES. (¶569.)

592. Heat a portion on Charcoal with blowpipe flame:

I—DEFLAGRATION indicates the presence of CHLORATES, NITRITES, NITRATES. †

(*a*)—If a CHLORATE—a portion of the dry substance, when treated with a few drops of Sulphuric Acid, will produce a yellow color and a chlorous odor. (Iodids and Bromids interfere with this test.)

(*b*)—If a NITRITE—a portion of the dry substance treated with a few drops of Sulphuric Acid, will produce effervescence with liberation of a brownish-red gas (NO_2) having a characteristic odor.

(*c*)—If a NITRATE OR NITRITE—the addition of Sulphuric Acid to a portion of dry substance, followed by the careful addition of a strong solution of Ferrous Sulphate, poured in the tube so as to form a layer, will produce a brown or purplish ring at the junction of the two fluids when cold. Upon heating it disappears. (Bromids, Iodids, Chlorates and Chromates interfere.)

II—CARBONIZATION indicates the presence of ORGANIC ACIDS. (Tartrates, Oxalates, Citrates and possibly Acetates, ¶594, 619.)

593. Treat a small portion of the dry substance in a test-tube with **diluted** Sulphuric Acid. Note whether effervescence takes place.

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* A very poisonous gas.

† If the original material was a solution, the test for Nitrates would be made on a portion of the original solution, since evaporation would drive off free Nitric Acid possibly present.

Effervescence and

- (*a*)—Odor of Hydrogen Sulphid (blackens Lead Acetate paper) indicates the presence of SULPHIDS. (¶554.)
- (*b*)—Odor of Sulphur Dioxid (odor of burning Sulphur) indicates the presence of SULPHITES, THIOSULPHATES. (¶440, 445.)
- (*c*)—Odor of Cyanogen* (colorless and odor of bitter almonds) indicates the presence of CYANIDS. (¶532.)
- (*d*)—Odor of Oxids of Nitrogen (brownish-red color and characteristic odor) indicates the presence of NITRITES. (¶559.)
- (*e*)—Chlorous odor and liquid turning yellow indicates the presence of CHLORATES and Hypochlorites. (Brownish-red = Bromates, BrO_3^-; Violet = Iodates, IO_3^-.) (¶564, 579.)
- (*f*)—No odor indicates the presence of CARBONATES, confirmed by passing the liberated gas thru Lime Water, which becomes turbid from formation of Calcium Carbonate. (¶481.)

594. Carry out Test 1 under ACETIC ACID, Page 163 on a portion of dry substance for ACETATES.

595. Carry out Test 2 under BORIC ACID, Page 143 on a portion of dry substance for BORATES.

596. Carry out Test 3 under HYDROFLUORIC ACID, Page 144 on a portion of dry substance for FLUORIDS.

597. Carry out Test 4 under SILICIC ACID, Page 145, on a portion of dry substance for SILICATES.

598. Change in color upon application of heat indicates OXIDS:

- (*a*)—If yellow when hot and white when cold, ZINC OXID, ZnO, is indicated.
- (*b*)—If orange-yellow when hot and yellowish when cold, LEAD OXID, PbO, or BISMUTH OXID, Bi_2O_3, are indicated.

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* A very poisonous gas.

(*c*)—If yellowish-brown when hot and yellow when cold, STANNIC OXID, SnO_2, is indicated.

II—Tests on a Solution of the Substance

599. Before testing for the Acids or Anions, the solution must be freed from Ammonium salts and then treated with Sodium Carbonate, if Metals other than those of the Alkali Group are present, since they will interfere with the tests for the Acids.

600. This may be done by adding an excess of a strong solution of Sodium Carbonate and boiling for 15 minutes. By this treatment Ammonia it gotten rid of and the Acids enter solution as Sodium salts, while the Metals form insoluble Carbonates or Oxids. Arsenic, if present, would be left as Arsenite or Arsenate. Filter, and use portions of the filtrate for the following tests, neutralizing where necessary. Save the precipitate, as it may be of use later. (See ¶616.)

601. (**A**) To one portion of filtrate add Nitric Acid, drop by drop, until just acid. Boil. This decomposes the carbonate with evolution of Carbon Dioxid which is completely expelled by boiling. If a slight precipitate forms, filter and reject the precipitate, since it consists merely of traces of metallic carbonates and hydroxids held in solution by excess of Sodium Carbonate. To a *portion* of the acid filtrate add SILVER NITRATE solution in slight excess.

(*a*)—If a precipitate forms the presence of one or more of the following are indicated:—CHLORIDS, BROMIDS, IODIDS, CYANIDS, FERROCYANIDS, FERRICYANIDS, THIOCYANATES, and SULPHIDS, Silver Nitrate solution is then added in excess to the *remainder* of the acid filtrate and the mixture filtered. The filtrate is saved for treatment described in (*d*).

(*b*)—If no precipitate forms upon the addition of Silver Nitrate, CHLORIDS, BROMIDS, IODIDS, CYANIDS, FERROCYANIDS, FERRICYANIDS, THIOCYANATES and SULPHIDS (are ABSENT and no further tests need be made for them. The liquid is treated as described in (*d*).

(*c*)—If a precipitate has been obtained by the addition of Silver Nitrate, the Tests described in ¶604–611 should be made on separate portions of the filtrate obtained by boiling with Sodium Carbonate and filtering.

(*d*)—Carefully pour on the filtrate from the Silver Nitrate precipitate, or the clear liquid in case no precipitate formed, Ammonium Hydroxid so as to form an alkaline layer over the acid fluid. There will be a neutral zone at the junction of the two layers in which a precipitate may form. If a precipitate forms, one or more of the following are indicated:—ARSENATES, ARSENITES, BORATES, CHROMATES, CITRATES, OXALATES, PHOSPHATES, TARTRATES.

(*e*)—If no precipitate forms by the above treatment ALL of these acids are ABSENT.

(*f*)—If a precipitate has formed at the junction of the two layers note the color of the same. ARSENATES give a reddish-brown precipitate; ARSENITES and PHOSPHATES, a yellow; CHROMATES, a purplish-red; and the others, white. On separate portions of the filtrate, obtained by boiling the original substance with Sodium Carbonate and filtering, the TESTS described in ¶613–619 should be made in order to determine which of the Acids indicated are present.

602. (**B**) To another portion of filtrate, obtained by boiling the original solution with Sodium Carbonate and filtering, add a sufficient quantity of Hydrochloric Acid to impart a neutral reaction. Filter if any slight precipitate forms. Boil to drive off the Carbon Dioxid evolved, and add a solution of BARIUM CHLORID.

(*a*)—The formation of a precipitate indicates the presence of SULPHATES, SULPHITES, THIOSULPHATES, PHOSPHATES, FLUORIDS, BORATES, AR-

SENATES, ARSENITES, CHROMATES, OXALATES, TARTRATES, and CITRATES.

(*b*)—If no precipitate forms ALL of these Acids are ABSENT.

(*c*)—If a precipitate forms add a slight excess of Hydrochloric Acid, and, if a white precipitate remains, the presence of a SULPHATE is shown. If all the precipitate dissolves the *absence of a* SULPHATE and the presence of one or more of the other acids mentioned in (*a*) is indicated. It must be borne in mind however that Thiosulphates are decomposed by Hydrochloric Acid with precipitation of Sulphur.

(*d*)—Separate portions of the filtrate, obtained by boiling the original solution with Sodium Carbonate and filtering, must be tested according to ¶613–622, in case a precipitate formed.

603. The following tests (¶604–611) are made if a precipitate has been produced by the addition of Silver Nitrate as described in ¶601.

604. CHLORIDS, if present ALONE, would be detected by applying Test 4 described under Hydrochloric Acid, Page 152.

605. BROMIDS, if present ALONE, would be detected by applying Test 4 described under Hydrobromic Acid, Page 153.

606. IODIDS, if present ALONE, would be detected by applying Test 4 described under Hydriodic Acid, Page 154.

607. CHLORIDS, BROMIDS and IODIDS, if present together, may be separated and identified as follows: Add diluted Sulphuric Acid to a portion of the filtrate (obtained by boiling with Sodium Carbonate and filtering), until neutral in reaction. Then add to a *portion* of this liquid some Copper Sulphate solution and sufficient SULPHUROUS Acid to impart a strong acid reaction. If a dirty-white precipitate forms, it consists of Cuprous Iodid and indicates the presence of IODIDS. If no precipitate forms, IODIDS are ABSENT. If a precipitate forms by the foregoing treatment, add to the remainder of the liquid sufficient Copper Sulphate solution and Sulphurous Acid to precipitate all of the Iodid as insoluble Cuprous Iodid. (If no precipitate has formed it is unnecessary to subject the remainder of the fluid to this treatment.) Filter off the precipitated Copper compound, and treat the filtrate with Potassium Hydroxid solution in order to precipitate the excess of Copper Sulphate as insoluble Copper Hydroxid. Filter again. Add a sufficient quantity of diluted Sulphuric Acid to the filtrate to neutralize and evaporate to dryness. Divide the residue obtained into two parts. Dissolve one part in water and add some Carbon Disulphid or Chloroform and Chlorin Water; the latter *drop by drop*. The presence of BROMIN is indicated by a reddish-brown color imparted to the Carbon Disulphid or Chloroform layer. Triturate the second part of the residue with half its weight of Potassium Dichromate, place the mixture in a small retort, and add some concentrated Sulphuric Acid. Apply a gentle heat. CHLORIN, if present, distils over as a deep, brownish-red gas—Chloro-chromic Anhydrid—which condenses to a liquid of the same color. Ammonium Hydroxid, added to the distillate, produces a yellow liquid from formation of Ammonium Chromate. If BROMIN, is present, and CHLORIN absent, the red distillate is decolorized by the Ammonium Hydroxid as explained under Hydrobromic Acid, ¶525.

608. CYANIDS and THIOCYANATES may be identified by applying the Tests described under Hydrocyanic and Thiocyanic Acids, Pages 154–156, on separate portions of the filtrate obtained by boiling the original solution with Sodium Carbonate and filtering.

609. FERROCYANIDS would be detected by adding an excess of Hydrochloric Acid to a portion of the filtrate and then some Ferric Chlorid solution. A dark blue precipitate of Ferric Ferrocyanid (Prussian Blue) indicates FERROCYANIDS.

610. FERRICYANIDS would be detected by adding an excess of Hydrochloric Acid to a portion of the filtrate and then some Ferrous Sulphate solution. A blue precipitate of Ferrous Ferricyanid (Turnbull's Blue) indicates FERRICYANIDS.

611. SULPHIDS (*most*) may be detected by warming a portion of the filtrate with Hydrochloric Acid. In the presence of a Sulphid, the evolved Hydrogen Sulphid gas is detected by its action on paper moistened with Lead Acetate solution.

612. The following Tests are carried out if a precipitate has been produced by the treatment described in ¶601 (*d*) and 602 (*d*):

613. ARSENATES and ARSENITES may be detected by applying the special tests for Arsenious and Arsenic Compounds described in Chapter VI, Pages 79–82, on small portions of the neutralized filtrate.

614. BORATES, in the absence of Copper, may be detected by the Sulphuric Acid and Alcohol Test described under Boric Acid, Chapter XVI, Page 143, on some of the original substance. If Copper is present, it must be first removed by precipitating it with Hydrogen Sulphid gas and filtering. The filtrate is then neutralized with Sodium Carbonate, evaporated to dryness, and the Borate test applied to the dried residue.

615. CHROMATES would be suspected if the filtrate after the Sodium Carbonate treatment is *yellow*. If yellow, make a portion of the filtrate acid with Acetic Acid and add some Lead Acetate solution. A yellow precipitate of Lead Chromate indicates the presence of CHROMATES. If the filtrate is *colorless*, CHROMATES are ABSENT.

616. CHROMIUM may have been found among the Metals. It is therefore necessary to determine whether it existed in the original substance as a Metal or Acid. If Chromates or Dichromates are present in the original substance, they are reduced by Hydrogen Sulphid and Ammonium Sulphid to Chromium salts, and Chromium would then be found in Group 4 as a Metal. Therefore a portion of the precipitate, obtained by boiling the original solution to be tested for the Acids with Sodium Carbonate, is dissolved in Hydrochloric Acid and tested for Chromium. If present in this precipitate, it proves the presence of Chromium as a Metal.

617. PHOSPHATES may be detected by making a portion of the filtrate acid with Nitric Acid, and applying the Ammonium Molybdate test described in Test 4 under Phosphoric Acid, Page 141.

618. OXALATES may be detected by adding Acetic Acid in excess to a portion of the filtrate, and then Calcium Sulphate solution. A white, finely divided precipitate indicates OXALATES.

619. TARTRATES, OXALATES and CITRATES would be indicated by the Tests carried out on the dry substance already described. If the test on dry substance gives positive indication of the presence of Organic Acids the following Tests may be made:

(*a*)—Add a slight excess of Hydrochloric Acid to a portion of the filtrate, obtained by boiling with Sodium Carbonate, and boil to expel the evolved Carbon Dioxid. Add Ammonium Hydroxid until slightly alkaline and then a slight excess of Calcium Chlorid solution. If no precipitate forms either at once or upon standing, TARTRATES and OXALATES are ABSENT. If a precipitate forms it may consist of Calcium TARTRATE or OXALATE. Therefore filter, set aside the filtrate, and wash the precipitate with water and allow it to drain. Next pour over it some cold Sodium Hydroxid solution. Calcium Tartrate is soluble in Sodium Hydroxid solution in the cold, but insoluble in the same when hot. (See Tartaric Acid, ¶504.) Filter and boil the filtrate. If a precipitate forms it indicates the presence of TARTRATES.

(*b*)—Any portion of the precipitate insoluble in cold Sodium Hydroxid solution may be examined for OXALATES, by decomposing it with concentrated Sulphuric Acid and passing the liberated gases thru some clear Lime Water.

(*c*)—CITRATES may be detected in the filtrate obtained in (*a*) above or in the fluid in which

Calcium Chlorid failed to produce a precipitate. Add to it some more Calcium Chlorid and boil. If a precipitate forms it indicates the presence of CITRATES, which may be confirmed by special tests. (¶508–512.)

620. SULPHATES may be detected by adding Hydrochloric Acid in excess to a portion of the filtrate and then Barium Chlorid solution. The formation of a white precipitate indicates the presence of SULPHATES.

621. SULPHITES and THIOSULPHATES may be tested for by adding some Sulphuric Acid to a portion of the original dry substance and noting whether effervescence takes place. If there is no effervescence, these acids, need not be looked for. If a gas is evolved, note the odor and make special tests for these acids on separate portions of the substance. (¶440–449.)

622. FLUORIDS would have been indicated by ¶596 under Tests on the Dry Substance.

TABLE IX.—FOR THE ACIDS OR ANIONS

I.—TESTS ON DRY SUBSTANCE (¶591). (If a solution is being examined, carefully evaporate to dryness on water-bath and use portions of residue for each test.

(A) Heat in dry tube:—(¶591.)
- **(1) Carbonization indicates $C_6H_5O_7^{---}$, $C_2O_4^{--}$, $C_4H_4O_6^{--}$, possibly $C_2H_3O_2^{-}$. (¶495, 508, 502, 583.)**
- **(2) Water Vapor indicates OH^- of heavy metals, or crystalline substances.**
- **(3) Liberation of a Gas indicates:**
  - **(*a*) If O:—ClO_3^-, IO_3^-, BrO_3^-, NO_3^- (and Peroxids). (¶579, 574.)**
  - **(*b*) If CO_2:—CO_3^{--}, HCO_3^-, $C_4H_4O_6^{--}$, $C_6H_5O_7^{---}$ and $C_2O_4^{--}$. (¶481, 495, 502, 508.)**
  - **(*c*) If SO_2:—SO_4^{--}, SO_3^{--}, S^{--} and $S_2O_3^{--}$. (¶436, 440, 445, 554.)**
  - **(*d*) If NO_2:—NO_2^- and NO_3^-. (¶559, 574.)**
  - **(*e*) If Cl, Br, or I:—Cl^-, Br^-, or I^-. (¶514, 520, 526, see also 607.)**
  - **(*f*) If $(CN)_2$:—CN^-. (¶532.)**
  - **(*g*) If H_2S:—S^{--}. (¶554.)**
  - **(*h*) If NH_3:—NH_4^- and CN^-. (¶532.)**
  - **(*i*) If PH_3:—$PH_2O_2^-$. (¶569.)**
- **(4) Change in Color indicates OXIDS. (¶598.)**
  - **(*a*) Yellow when hot, white when cold indicates ZnO.**
  - **(*b*) Orange-yellow when hot, yellow when cold indicates PbO or Bi_2O_3.**
  - **(*c*) Yellowish-brown when hot, yellow when cold indicates SnO_2.**

TABLE FOR THE ACIDS OR ANIONS—Continued

(B) Heat on Charcoal with blowpipe:—(¶592.)
(1) Deflagration indicates ClO_3^-, NO_3^-, NO_2^-. (¶579, 574, 559.)
(2) Carbonization indicates $C_6H_5O_7^{---}$, $C_4H_4O_6^{--}$, $C_2O_4^{--}$, possibly $C_2H_3O_2^-$. (¶ 495, 508, 502, 583.)

(C) Treat with diluted H_2SO_4:—(¶593.)
(1) Effervescence and odor of H_2S indicates S^{--}. (¶554.)
(2) Effervescence and odor of SO_2^{--} indicates SO_3^{--} and $S_2O_3^{--}$. (¶440, 445.)
(3) Effervescence and odor of $(CN)_2$ indicates CN^-. (¶532.)
(4) Effervescence and odor of NO_2 indicates NO_2^-. (¶559.)
(5) Effervescence and odor of Cl indicates ClO_3^-, and ClO^-. (¶579, 564.)
(6) Effervescence and *no* odor indicates CO_3^{--}. (¶481.)

(D) Carry out the following:—(¶594–597.)
(1) Test 1 under Acetic Acid for $C_2H_3O_2^-$. (¶584.)
(2) Test 2 under Boric Acid for BO_3^{---}. (¶469.)
(3) Test 3 under Hydrofluoric Acid for F^-. (¶475.)
(4) Test 4 under Silicic Acid for SiO_3^{--}. (¶480.)

II.—TESTS ON SOLUTION:—Boil with Na_2CO_3, filter. Save precipitate for Cr, ¶616. Test **portions** of filtrate as follows:—(¶599–600.)

(A) Add HNO_3 until acid; to a portion of this add $AgNO_3$ in slight excess. If precipitate forms, add $AgNO_3$ in excess to remainder and filter. (¶601 (A).)

(1) PRECIPITATE:—The formation of a precipitate indicates one or more of the following:— Cl^-, Br^-, I^-, CN^-, $Fe(CN)_6^{----}$, $Fe(CN)_6^{---}$, CNS^-, and S^{--}. (¶601 (*a*), & (*c*); 604–611.) If *no* precipitate forms, the foregoing are ABSENT. (¶601 (*b*).)	(2) FILTRATE:—Pour on NH_4OH to form a layer. If a precipitate forms at the junction of the layers, one or more of the following are indicated: AsO_4^{---}, AsO_3^{---}, BO_3^{---}, CrO_4^{--}, $C_6H_5O_7^{---}$, $C_2O_4^{--}$, PO_4^{---}, $C_4H_4O_6^{--}$. (¶601 (*d*) & (*f*).) (¶613–619.) If *no* precipitate forms the foregoing are ABSENT. (601 (*e*).)

(B) Add enough HCl to make neutral. Filter. Boil and then add $BaCl_2$.
(1) The formation of a precipitate indicates one or more of the following:—(¶602 (B).)
SO_4^{--}, SO_3^{--}, $S_2O_3^{--}$, PO_4^{---}, F^-, BO_3^{---}, AsO_4^{---}, AsO_3^{---}, CrO_4^{--}, $C_2O_4^{--}$, $C_4H_4O_6^{--}$, $C_6H_5O_7^{---}$. (¶613–622.)
(2) In presence of a precipitate, add slight excess HCl. If a WHITE precipitate remains, SO_4^{--} is indicated. (¶602 (*c*).)
(3) If *no* precipitate forms, the foregoing are ABSENT. (¶602 (*b*).)

(C) If $AgNO_3$ (A) and $BaCl_2$ (B) fail to produce precipitates, test for NO_3 (Page 161), ClO_3^- (Page 162), and $C_2H_3O_2^-$ (Page 163).

PART III

CHAPTER XX

The Analysis of an Unknown

623. After a qualitative examination of a substance, the analyst should be able to report not only what elements are contained therein, but also the relative amounts that are present. Thus, if Calcium Chlorid is the substance under examination and Magnesium Chlorid and Aluminium Chlorid are also found in very small amounts, the report should read: "Substance examined is Calcium Chlorid containing traces of Magnesium and Aluminium Chlorids." However, in order to do this the student must start with a known quantity of the substance under examination (0.5 to 1.0 Gm.), and compare the amount of the precipitates produced, the depth of color, etc. He will be able to estimate the amount of a precipitate obtained in an analysis if he has studied the actions of the elements with known amounts of the different materials. If in doubt, he can take varied amounts of a solution of known strength and carry out the identification test with these and then make a comparison. It should be remembered that such comparisons are but roughly approximate.

624. Every analysis should be divided into three parts:

I. PRELIMINARY EXAMINATION.
II. EXAMINATION FOR THE METALS (BASES OR CATIONS).
III. EXAMINATION FOR THE ACIDS (OR ANIONS).

625. The substance under examination may be one of the following:

A. A GAS.
B. A SOLUTION or a LIQUID.
C. A SOLID, but *non-metallic*.
D. A SOLID, which is a metal or an alloy. (See Chapter XXI, Page 184.)

626. It is well for the student to use a form, somewhat like the one on the following page, noting each step taken, the

No. of Substance........................ *Student's Name*.. *Received*........................ 19..........

I. Preliminary Observations.. *Reported*........................ 19..........

No.	Substance.	Reagent.	Result.	Inference.	Precipitate or Residue.	Solution or Filtrate.	Remarks.
1							
2							
3							
4							
5							
6							
7							
8							
9							
10							
11							
12							
13							
14							
15							

Found—II. Cations:.. *III. Anions:*..

IV. Probable Combinations:..

631. *If a solution,* a portion is prepared for the precipitation of Group 1 and the rest of the metallic groups. Ferrocyanids (¶542); Ferricyanids (¶548); Oxalates (¶495); Phosphates (¶450); and Tartrates (¶502); interfere, especially with the precipitations by Hydrogen Sulphid and Ammonium Sulphid, and must therefore be removed if present. This is done by evaporating the solution to dryness, and fusing the residue with about five times as much Ammonium Nitrate (*in a hood*). Then cool, extract with diluted Nitric Acid, and proceed with the systematic examination for the Metals beginning with Table I, Page 57, remembering that Potassium and Iron are present as decomposition products from the Cyanids. If there is any residue insoluble in the dilute Nitric Acid, treat it according to ¶633 (C) "*if the unknown is a solid.*" If Ferrocyanids or Ferricyanids are not present, test the reaction of the solution. If it is acid, proceed with the examination for the Metals or Cations, beginning with Table I, Page 57. If the solution is alkaline, acidify with Nitric Acid and examine for the Metals or Cations beginning with Table I, Page 57. If the addition of Nitric Acid produces a precipitate, dissolve it with a slight excess of Nitric Acid, warming if necessary; if this precipitate is insoluble in Nitric Acid, treat it according to ¶633 (C) "*if the unknown is a solid.*"

632. *If a liquid* and *not a solution,* pour a portion of it into some water and convert it into a solution in this fashion if possible, and examine the resulting solution for the Metals or Cations beginning with Table I, Page 57. If a precipitate forms upon adding the liquid to water, filter it out and treat it according to ¶633 (C) "*if the unknown is a solid.*"

633. (C) If the unknown is a Solid but non-metallic: Examine the solutions obtained by the treatment with water, Hydrochloric Acid, Nitric Acid, and Nitro-hydrochloric Acid described in ¶630 (*d*), for the Metals or Cations as follows:

634. (1) *The Aqueous Solution.*—If any of the substance has dissolved in the water, test the reaction of the solution with litmus. If it is neutral or acid, proceed with the Examination for the Metals or Bases, beginning Table I, Page 57. If alkaline, make the solution *slightly* acid by adding a *few drops of* Nitric Acid. If a precipitate forms, test a small portion of it with Nitric Acid and if it dissolves, decant the liquid and add enough Nitric Acid to the precipitate to redissolve it. Then add it to the decanted liquid. If the precipitate does not dissolve in the Nitric Acid, filter it out, wash it with water and treat it as a solid insoluble in water. The acid solution is then examined for the Metals or Bases, beginning Table I, Page 57.

635. (2) *The Hydrochloric Acid Solution.*—The residue left after the hot water treatment is boiled with hot Hydrochloric Acid. At this point there may be indications of the presence of certain Acids or Anions. (See ¶593.) If the treatment with Hydrochloric Acid seems to precipitate the Chlorids of the members of Group 1 of the Metals, the treatment with Nitric Acid should be carried out first. [¶630 (*d*).] The Hydrochloric Acid solution cannot contain the members of Group 1, excepting Lead, unless a too concentrated acid is used, in which case Silver Chlorid will dissolve to some extent. Any Silver that has been dissolved, will be reprecipitated by diluting the solution with about three times its volume of water. If such is the case, remove the precipitate by filtration and test it for Silver. (¶46.) The Hydrochloric Acid solution is then proceeded with as in the case of the Aqueous Solution beginning, of course, with the precipitation of Group 2, beginning with ¶100, Page 72.

636. (3) *The Nitric Acid Solution.*—If the treatment of the substance with Nitric Acid has preceded the treatment with Hydrochloric Acid, the members of Group 1 of the Metals have been dissolved, and Hydrochloric Acid should be added to completely precipitate the members of this group (Group 1). The precipitated Chlorids of the members of Group 1 of Metals are filtered off and analyzed, and the filtrate treated in the usual fashion for the members of Group 2 of the Metals and the rest of the metallic groups.

637. (4) *The Nitrohydrochloric Acid Solution.*—Boil the solution to expel the excess of acid and the Nitrosyl Chlorid, evaporate with Hydrochloric Acid to insure the complete decomposition of any remaining Nitric Acid, and then dilute with three times as much water in order to precipitate any metals of Group 1 present. Filter off any precipitate and examine it for Group 1 of the Metals, and proceed with the filtrate in the regular order for the other metallic groups.

638. NOTE.—The above solutions may frequently be combined and the resulting mixture analyzed for the Metals or Bases. This should be determined by mixing small portions of each of the solutions to see whether precipitation takes place. If no precipitate forms, mix the rest of the solutions and proceed with the Examination for the Metals or Bases. If a precipitate forms which is soluble in an excess of Hydrochloric Acid upon warming and which does not reprecipitate upon cooling (the precipitate of Lead Chlorid, $PbCl_2$, does not interfere), the solutions may be mixed. If the precipitate is not soluble in Hydrochloric Acid, add Hydrochloric Acid to the Aqueous Solution and also to the Nitric Acid Solution and carry out the analysis of any precipitate formed for the presence of the members of Group 1 of the Metals. Then add the Hydrochloric Acid solution and the Nitrohydrochloric Acid Solution to the combined filtrates from the first two solutions. If no precipitate is formed by this combination, boil off the Nitric Acid, displacing it with Hydrochloric Acid, and proceed in the usual fashion. If a precipitate is produced, each solution must be analyzed separately.

Table X will be of assistance to the student in studying the solubilities of various substances.

III—Examination for the Acids (or Anions)

(A) If the unknown is a GAS, consult the instructor.

(B) If the unknown is a SOLUTION or a LIQUID:

639. IF A SOLUTION: *First.*—Evaporate a portion to dryness on a water-bath and carry out ¶590–598, "Tests on Dry Substance," Pages 165–168.

Second.—Use another portion for "Tests on a Solution of the Substance," ¶599–622, Pages, 168–174.

640. If a Liquid, ***not a solution,*** cautiously pour some of it into water and if it gives a clear solution, proceed with it as with "If a solution," ¶639 above. If a precipitate is also obtained, treat it as with "*If the unknown is a solid,*" ¶641–42.

641. (C) If the unknown is a Solid but non-metallic: *First.*—Carry out "Tests on Dry Substance," ¶590–598, Pages, 165–168.

642. *Second.*—If the unknown is *soluble in water,* make a solution, using from 0.5 to 1.0 Gm. of solid, in water and carry out "Tests on a Solution of the Substance," ¶599–622, Pages, 168–174. *If the unknown is insoluble in water,* fuse it thoroughly with Sodium Carbonate, powder the resulting mass, and boil it with water to dissolve. Filter, neutralize and use the filtrate for "Tests on a Solution of the Substance," beginning with ¶601–622, Page 168. The insoluble residue may be examined for the Metals or Cations if this has not already been done. (¶644.)

643. If the Unknown is Insoluble in Water and in Acids, it may contain the following substances: Barium Sulphate, Strontium Sulphate, Calcium Sulphate, Calcium Fluorid, Silver Chlorid, Silver Bromid, Silver Iodid, Silver Cyanid, Lead Sulphate. Analysis may be carried out as follows:

Fuse the unknown with Sodium Carbonate, powder the resulting mass and boil it with water to dissolve. Filter, neutralize the filtrate, and carry out the examination for the Acids or Anions, beginning with ¶601–622.

644. The residue insoluble in the water, which contains the Metals or Cations as Carbonates or Oxids, is dissolved in Nitric Acid, diluted with water and examined for the Metals or Cations, beginning with Table I, Page 57.

CHAPTER XXI

The Analysis of a Metal or an Alloy

645. The analysis of A METAL OR AN ALLOY is much more simple than the analysis of a mixture of salts, because no Acids or Anions are tested for. Of the non-metallic elements, Carbon, Sulphur, Phosphorus and Silicon are the only ones usually considered.

646. All of the common metals, with the exception of Gold, Platinum, Antimony and Tin, are soluble in Nitric Acid. Alloys are usually soluble in Nitric Acid also, and in the few cases which are not soluble in this acid, Nitrohydrochloric Acid will usually effect solution. However, some alloys are rich in Silicon and these are extremely difficult to dissolve, even in Nitrohydrochloric Acid. In such cases it is best to fuse with a caustic alkali and then dissolve the "melt" in Nitric Acid. It is inadvisable to dissolve an alloy in Hydrochloric Acid as the non-metallic elements Carbon, Sulphur, Phosphorus and Silicon in the form of Carbids, Sulphids, Phosphids, and Silicids, as well as Arsenids, may be present in small amounts and are decomposed by Hydrochloric Acid escaping as volatile Hydrogen compounds.

647. For ordinary alloys the following method may be used:

Treat from 1 to 2 Gm. of the unknown (in the form of borings), contained in a porcelain dish, under a hood, with about 20 Cc. of a mixture of equal parts of concentrated Nitric Acid and water. After the first violent action has ceased, carefully evaporate the mixture, *on a water-bath*, stirring constantly, almost to dryness. (Do not overheat or insoluble basic salts may form, as shown by the dark color of the residue. Should this happen add a little more concentrated Nitric Acid, heat the mixture somewhat, dilute with water, and evaporate again.) Next add some water and warm the mixture. The result may be:

(A) A clear solution.

(B) A solution containing a white or greenish residue.

648. (A) *If a clear solution is obtained*, the alloy contains no Tin or Antimony. Examine the solution for the Metals or Cations beginning with Table I, Page 57.

649. (B) *If a solution containing a residue is obtained*, filter the mixture, and evaporate a little of the filtrate on a water-bath to determine whether any of the substance has been dissolved. If no residue is secured upon evaporation, the filtrate is discarded. If a residue is obtained upon evaporation of the filtrate, proceed with the analysis for the Metals or Cations, beginning with Table I, Page 57.

650. The residue, insoluble in Nitric Acid, may contain Tin Oxid, SnO_2; Antimony Oxid, Sb_2O_3 or Sb_2O_5; Bismuth Oxid, Bi_2O_3; Phosphorus Pentoxid, P_2O_5; and traces of Iron, Lead, Copper, etc. Wash the residue with water, add some Potassium Hydroxid solution to make alkaline, and then about 10 Cc. of Potassium Sulphid solution. Heat the mixture for some time *on a water-bath* and then filter. This gives a residue and a filtrate.

651. The residue may contain Bismuth Sulphid, Bi_2S_3; Ferrous Sulphid, FeS; Lead Sulphid, PbS; Copper Sulphid, CuS, etc. Dissolve this residue in dilute Nitric Acid and examine the resulting solution for the Metals or Cations, beginning with Table I, Page 57.

652. The filtrate may contain K_2SnS_3, K_3SbS_3 and K_3PO_4. Dilute this filtrate with water, and add enough Hydrochloric Acid to give the mixture an acid reaction. Then filter. The precipitate obtained may contain Tin Sulphid, SnS_2 and Antimony Sulphid, Sb_2S_3 or Sb_2S_5. The filtrate may contain Potassium Dihydrogen Phosphate, KH_2PO_4, and Potassium Chlorid, KCl.

653. Dissolve the precipitate in concentrated Hydrochloric Acid, boil, dilute with a little water, filter out any

TABLE XI.—FOR ALLOYS

<table>
<tr><td colspan="4">Treat 1 to 2 Gm. of alloy under a hood with about 20 Cc. HNO_3 (1–1); carefully evaporate on water-bath almost to dryness, avoiding overheating. Add some water and warm. (¶645–647.) Result is (A) or (B).</td></tr>
<tr><td colspan="4">(A) IF A CLEAR SOLUTION:—Examine for the Metals or Cations beginning with Table I, Page 57. Sn and Sb need <i>not</i> be tested for. (¶648.)</td></tr>
<tr><td colspan="4">(B) IF A SOLUTION CONTAINING A WHITE TO GREENISH RESIDUE:—Filter. (¶649.)</td></tr>
<tr><td colspan="3">(<i>a</i>) RESIDUE:—May contain SnO_2, Sb_2O_3 or Sb_2O_5, Bi_2O_3, P_2O_5, and traces of Fe, Pb, Cu, etc. Wash with water; add KOH till alkaline; and then 10 Cc. of K_2S. Heat for some time on water-bath and filter. (¶650.)</td><td rowspan="3">(<i>b</i>) FILTRATE:—Test for the Metals or Cations beginning Table I, Page 57. (¶649.)</td></tr>
<tr><td rowspan="2">(<i>a</i>) RESIDUE:—May contain Bi_2S_3, FeS, PbS, CuS, etc. Dissolve in dil. HNO_3, filter, and test for the Metals or Cations, beginning Table I Page 57. (¶651.)</td><td colspan="2">(<i>b</i>) FILTRATE:—May contain K_2SnS_3, K_3SbS_3 and K_3PO_4. Dilute with water, add HCl till acid, and filter. (¶652.)</td></tr>
<tr><td>(<i>x</i>) PRECIPITATE:—May contain SnS_2 and Sb_2S_3 or Sb_2S_5. Dissolve in conc. HCl; boil; dilute with H_2O; filter; test for Sn and Sb according to Table IV, Group 3, Page 93. ¶653.)</td><td>(<i>y</i>) FILTRATE:—May contain KH_2PO_4 and KCl. Evaporate to small bulk; add NH_4OH in excess and then Mg. Mixture. A WHITE CRYSTALLINE precipitate indicates PHOSPHORUS. (¶654.)</td></tr>
</table>

precipitated Sulphur, and examine for Tin and Antimony as in Table IV, Group 3, Page 93.

654. Evaporate the filtrate from ¶652 to small bulk, add an excess of Ammonium Hydroxid, and finally some Magnesia Mixture. A ***white crystalline precipitate*** of Magnesium Ammonium Phosphate, $MgNH_4PO_4$, indicates the presence of PHOSPHORUS in the original substance.

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Nervous and Mental Diseases, Children, Hygiene, and Medical Jurisprudence

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Clinical Manual of Mental Diseases. By FRANCIS X. DERCUM, PH. D., M. D., Professor of Nervous and Mental Diseases at Jefferson Medical College, Philadelphia. Octavo ot 479 pages. Cloth, $3.50 net.

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Nervous and Mental Diseases. By ARCHIBALD CHURCH, M. D., Professor of Nervous and Mental Diseases and Medical Jurisprudence, Northwestern University Medical School, Chicago; and FREDERICK PETERSON, M. D., formerly Professor of Psychiatry at the College of Physicians and Surgeons, N. Y. Handsome octavo, 944 pages; 350 illustrations. Cloth, $5.00 net. **October, 1914**

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Kaplan's Serology of Nervous and Mental Diseases

Serology of Nervous and Mental Diseases. By D. M. KAPLAN, M. D., Director of Clinical and Research Laboratories, Neurological Institute, New York City. Octavo of 346 pages, illustrated. Cloth, $3.50 net. **Published June, 1914**

This is an entirely new work, giving you the indications, contra-indications, preparation of patients, technic, after-phenomena, after-care, and disposal of the fluids obtained by lumbar puncture. You get a full discussion of the serology of all nervous and mental diseases of *non-luetic* etiology (including disorders of *internal secretion*), and of every type of *luetic* nervous and mental disease, giving the *Wassermann reaction in detail,* the use of *salvarsan* and *neosalvarsan,* etc.

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Herrick and Crosby's Laboratory Neurology

A Laboratory Outline of Neurology. By C. JUDSON HERRICK, PH. D., Professor of Neurology, University of Chicago; and ELIZABETH C. CROSBY, PH. D., Principal of the High School, Petersburg, Mich. 12mo of 120 pages, illustrated. Cloth, $1.50 net. **Published January, 1917**

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Second Edition published May, 1914

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To the general practitioner, who first sees these "borderline" cases (the neuroses and the psychoses), as well as to those specially interested in neurologic work, Dr. Brill's work will prove most valuable. Dr. Brill has had wide clinical experience, both in America and in Europe. The results of this experience you get in this book. Here you get the practical application of all Freud's theories—and from the pen of a man thoroughly competent to write.

Hunt's Diagnostic Symptoms of Nervous Diseases

Diagnostic Symptoms of Nervous Diseases. By EDWARD L. HUNT, M. D., formerly Instructor in Neurology and Assistant Chief of Clinic, College of Physicians and Surgeons, New York. 12mo of 292 pages, illustrated. Cloth, $2.00 net. **Second Edition published June, 1917**

Stiles on the Nervous System

The Nervous System and its Conservation. By PERCY G. STILES, Instructor in Physiology at Harvard University. 12mo of 240 pages, illustrated. Cloth, $.150 net. **Second Edition published November, 1914**

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Practice of Pediatrics. By CHARLES GILMORE KERLEY, M. D., Professor of Diseases of Children, New York Polyclinic Medical School and Hospital. Octavo of 913 pages, illustrated. Cloth, $6.50 net.

Published January, 1918

SECOND EDITION

This work is not a cut-and-dried treatise—but the *practice* of pediatrics, giving fullest attention to *diagnosis* and *treatment*. The chapters on the newborn and its diseases, the feeding and growth of the baby, the care of the mother's breasts, artificial feeding, milk modification and sterilization, diet for older children—from a monograph of 125 pages. Then are discussed in detail every disease of childhood, *telling just what measures should be instituted*, what drugs given, *60 valuable prescriptions* being included. The chapter on *vaccine therapy* is right down to the minute, including every new method of proved value—with the exact technic. There is an excellent chapter on *Gymnastic Therapeutics*. Another feature consists of *the 165 illustrative cases—case teaching* of the most practical sort.

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CLINICAL LECTURES IN INFANT FEEDING. By LEWIS WEBB HILL, M. D., Alumni Assistant in Pediatrics, Harvard Medical School, and JESSE R. GERSTLEY, M. D., Instructor in Pediatrics, Northwestern University Medical School. 12mo of 377 pages, illustrated. Cloth, $2.75 net. **Published October, 1917**

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Abt's Preparation of Infants' Foods

THE PREPARATION OF INFANTS' FOODS. By ISAAC A. ABT, M. D., Professor of Diseases of Children, Northwestern University Medical School. 12mo of 143 pages. Cloth, $1.25 net. **Published July, 1917**

This is a practical guide for infant feeding, giving to young mothers, nurses, and caretakers minute directions on the preparation of food for infants and young children. You get weights and measures; the mineral constituents and caloric values of foods. You get such practical material as diet-lists for constipation in older children, an outline of a plan for feeding babies, care of nipples and bottles, etc., and a great host of recipes for beverages of all kinds, milk preparations, soups and broths, puddings and cereal preparations, custards, eggs, vegetables, fruits, meats, sea foods, and breads.

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A Manual of Diseases of Children. By JOHN RUHRÄH, M. D., Professor of Diseases of Children, College of Physicians and Surgeons, Baltimore. 12mo of 552 pages, fully illustrated. Flexible leather, $2.75 net.

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In revising this work for the fourth edition Dr. Ruhräh has carefully incorporated all the latest knowledge on the subject. All the important facts are given concisely and explicitly, the therapeutics of infancy and childhood being outlined very carefully and clearly. There are also directions for dosage and prescribing, and many useful prescriptions are included.

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Published July, 1914

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Bergey's Hygiene

The Principles of Hygiene: A Practical Manual for Students, Physicians, and Health Officers. By D. H. BERGEY, A. M., M. D., Assistant Professor of Bacteriology in the University of Pennsylvania. Octavo volume of 543 pages, illustrated. Cloth, $3.50 net.

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This book is intended to meet the needs of students of medicine in the acquirement of a knowledge of those principles upon which modern hygienic practises are based, and to aid physicians and health officers in familiarizing themselves with the advances made in hygiene and sanitation in recent years. This fifth edition has been very carefully revised, and much new matter added, so as to include the most recent advancements.

Buffalo Medical Journal

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A MANUAL OF PERSONAL HYGIENE: Proper Living upon a Physiologic Basis. By Eminent Specialists. Edited by WALTER L. PYLE, A. M., M. D., Assistant Surgeon to Wills Eye Hospital, Philadelphia. Octavo volume of 555 pages, fully illustrated. Cloth, $1.75 net.

The book has been thoroughly revised for this new edition, and a new chapter on Food Adulteration by DR. HARVEY W. WILEY added. There are important chapters on Domestic Hygiene and Home Gymnastics, Hydrotherapy, Mechanotherapy, and First Aid Measures.

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Golebiewski and Bailey's Accident Diseases

Atlas and Epitome of Diseases Caused by Accidents. By DR. ED. GOLEBIEWSKI, of Berlin. Edited, with additions, by PEARCE BAILEY, M. D., Consulting Neurologist to St. Luke's Hospital, New York. With 71 colored illustrations on 40 plates, 143 text illustrations, and 549 pages of text. Cloth, $4.00 net. *In Saunders' Hand-Atlas Series.* **Published 1901**

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Atlas of Legal Medicine. By DR. E. VON HOFMANN, of Vienna. Edited by FREDERICK PETERSON, M. D., Professor of Psychiatry in the College of Physicians and Surgeons, New York. With 120 colored figures and 193 half-tone illustrations. Cloth, $3.50 net. **Published April, 1898**

Jakob and Fisher's Nervous System

Saunders' Atlases

Atlas and Epitome of the Nervous System and Its Diseases. By PROFESSOR DR. CHR. JAKOB, of Erlangen. Edited, with additions, by EDWARD D. FISHER, M. D., University and Bellevue Hospital Medical College. With 83 plates and copious text. Cloth, $3.50 net. **Published 1901**

Spear's Nervous Diseases

Published November, 1916

A Manual of Nervous Diseases. By IRVING J. SPEAR, M. D,. Professor of Neurology at the University of Maryland, Baltimore. 12mo of 660 pages› illustrated. Cloth, $3.00 net.

This is a comprehensive digest, supplying the means to a clear understanding of neurology, and robbing that subject of much of its difficulty. You are given, first, a brief description of the practical anatomy and physiology, with those facts and theories that bear on the mechanism of organic nervous diseases. Then pathology is given, the simpler diseases being considered first, gradually preparing the reader to grasp the more difficult ones. The descriptions are clear and brief, *differential diagnoses* and *treatments* being brought out very definitely. Only the most recent accepted facts have been considered. For the treatments recommended, no special apparatus is required beyond a galvanic and faradic battery; they demand no special training, and they are easily remembered.

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"Clearly and intelligently written; we have noted few inaccuracies and several suggestive points. Some affections unmentioned in many of the large text-books are noted." —*Boston Medical and Surgical Journal.*

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PERSONAL HEALTH: A Doctor Book for Discriminating People. By WILLIAM BRADY, M.D., Elmira, N. Y. 12mo of 406 pages. Cloth, $1.50 net.

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ATLAS AND EPITOME OF DISEASES OF CHILDREN. By DR. R. HECKER and DR. J. TRUMPP, of Munich. Edited, with additions, by ISAAC A. ABT, M.D., Assistant Professor of Diseases of Children, Rush Medical College, Chicago. With 48 colored plates, 144 text-cuts, and 453 pages of text. Cloth, $5.00 net. **Published April, 1907**

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